DOE-GO-14154-1
OHIO FINAL report Velocys 30Sept08
Covering Period February 2, 2004 to June 30, 2008
Date of Report September 30, 2008

Award Number:	DE-FC36-04GO14154
Project Title:	Olefins by High-Intensity Oxidation (OHIO)
Project Period:	2 February 2004 – 30 June 2008
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Executive Summary

The overall goal of the OHIO project was to develop a commercially viable high intensity process to produce ethylene by controlled catalytic reaction of ethane with oxygen in a microchannel reactor. Microchannel technology provides a breakthrough solution to the challenges identified in earlier development work on catalytic ethane oxidation. Heat and mass transfer limitations at the catalyst surface create destructively high temperatures that are responsible for increased production of waste products (CO, CO_2, and CH_4).

The OHIO project focused on microscale energy and mass transfer management, designed to alleviate these transport limitations, thereby improving catalyst selectivity and saving energy-rich feedstock. The OHIO project evaluated ethane oxidation in small scale microchannel laboratory reactors including catalyst test units, and full commercial length single- and multi-channel reactors. Small scale catalyst and single channel results met target values for ethylene yields, demonstrating that the microchannel concept improves mass and heat transport compared to conventional reactors and results in improved ethylene yield.

Earlier economic sensitivity studies of ethane oxidation processes suggested that only modest improvements were necessary to provide a system that provides significant feedstock, energy, and capital benefits compared to conventional steam ethane cracking. The key benefit derived from the OHIO process is energy savings. Ethylene production consumes more energy than any other U.S. chemical process.[1] The OHIO process offers improved feedstock utilization and substantial energy savings due to a novel reaction pathway and the unique abilities of microchannel process technology to control the reaction temperature and other critical process parameters. Based on projected economic benefits of the process, the potential energy savings could reach 150 trillion Btu/yr by the year 2020, which is the equivalent of over 25 million barrels of oil.

Project Accomplishments

The following summarizes the specific objectives from the initial proposal, and a summary statement of the project accomplishments against those objectives:

1. Adapt computational reactor models to design the geometry and evaluate the performance of a microchannel reactor with improved selectivity and/or productivity in the catalytic oxydehydrogenation of ethane to ethylene.
   - A preliminary computational model of the reactor was developed and reconciliation of the kinetic functions was completed, meeting a project milestone.
2. Design, build and test single- and multi-channel MPT reactors for ethane oxydehydrogenation that demonstrate the performance needed for a commercial demonstration.
   - Mod 1 and 2 reactors that include a single full commercial length microchannel were designed, built and operated with high flow rates for more than 100 hours in a continuous run, meeting a project milestone.
   - A multi-channel reactor was designed, built and successfully operated with no apparent buildup of coke or increase in pressure drop, meeting a project milestone. Conversion of ethane and selectivity to ethylene in the reactor nearly matched those observed with the same catalyst in coupon tests. Acetylene production was unusually low.
3. Demonstrate at the laboratory scale the improved catalytic performance needed to achieve economic advantage and energy savings.
   - Adaptation of the conventional fixed bed catalysts to microchannel geometry was demonstrated in small laboratory reactors, meeting the first project milestone.
   - Several stabilized catalyst formulations were developed that gave good performance with minimal coke formation and little change in composition with time, meeting a project milestone.
4. Develop integrated process flowsheets including conversion, separation, recovery and utilities that optimize the advantages of the OHIO process.
   - Dow developed a process flowsheet to compare to conventional ethylene processes and identified the advantages of the OHIO process as being largely in the energy/feedstock savings.
5. Determine the most effective means to retrofit existing ethylene plants.
   - This objective was deferred when the budget was reduced by limitations of funds from DOE.
6. Calculate the capital and operating costs of the high intensity MPT ethylene process and compare to conventional processes.
   - A preliminary economic evaluation of the process was completed that shows advantages in both CAPEX and OPEX for the new process compared to conventional ethane cracking, meeting a project milestone.

Task 1 – Economic Evaluation

The process portion (minus utilities) of the flowsheet was coded and evaluated using ASPEN modeling. Experimental data from the laboratory tests was used, and estimates of the minor components were completed. The data were incorporated and material and energy balances were achieved. Several unit operations separately represented in the flowsheet were successfully integrated into the microchannel reactor. Preliminary results showed the expected savings on ethane and fuel feeds are greater than the added cost of oxygen and reduction in byproduct credits, for a net operating cost savings. Capital costs are also some 5-10% lower with the microchannel system than with conventional technology.

As expected the advantages in operating costs are dependent on the conversion of ethane, utilization of oxygen, and yield of ethylene. In addition, the product valuations are important. Addition of the product slates produced by the smaller components in a real ethane feed (eg propane, butane) was done based on conventional product slates. NPV was calculated for two cases showing a significant improvement for the microchannel technology compared to the conventional cracking process.

Task 2 – Adapt Catalyst to Microchannel Geometry

Catalyst integration to the reactor channel walls involves wall pre-treatment, coating with the support and catalyst, stabilization and activation. One candidate for reactor material evaluated was an oxide coated alloy which can withstand corrosion under wet oxidizing conditions inherent in any oxidation processes. The challenge arises with the fact that the pre-treated surfaces have low porosity and are free of chemically active surface groups which consequently reduces the ability to anchor a catalytic material to the wall surface. Efforts were made to increase the chemical reactivity by increasing the surface porosity by changing treatment protocols on the precursor surfaces.

In a typical experiment a standard alloy coupon with about 0.3 in^2 of geometric area was coated with the precursor material. Coupons of this type are pre-treated using one of a variety of protocols to develop the surface to which the catalyst will be attached. The pretreatment protocol was optimized with respect to temperature, time, atmosphere, and additives. Evaluation of the pretreatment quality was accomplished by SEM analysis of the surface morphology and chemistry, and by corrosion testing.

Microscopic images of three coupons shown in Figure 1(a-c) show variations in surface morphology and porosity as a function of treatment.

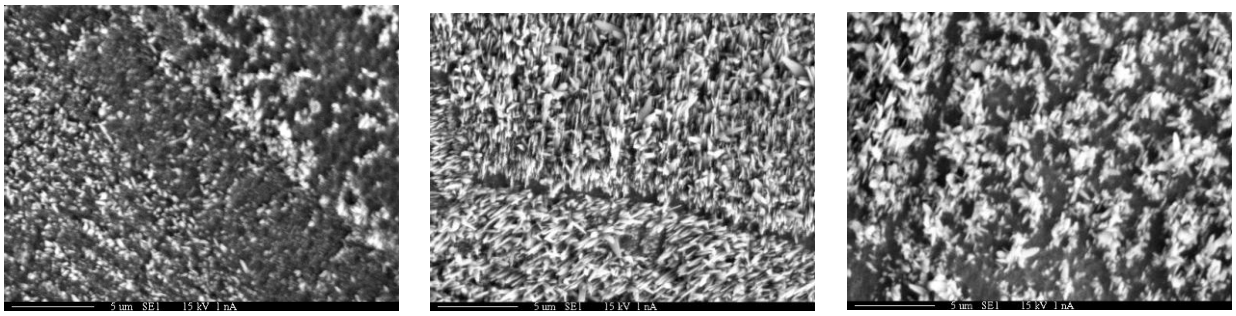

Figure 1. Microscopic images of three coupons with variations in surface morphology and porosity as a function of treatment.

Coating procedures were evaluated for the introduction of the catalyst support and active metal(s). Figure 2 shows the variation of the alumina sol uptake with the number of coating on 4 standard coupons. After four coatings, an increase in weight gain was still being observed. The highest weight gain attained was 6.5mg/in^2. When an additive was applied before the sol coating, the initial sol uptake was dramatically increased to as much as 14mg/in^2, as shown in Figure 3 In all cases, the additive uptake alone was approximately 10% of the initial weight gain. When the additive was applied prior to sol coating, all four samples showed an increase in weight gain through the 2nd coating of alumina sol; however, they all experienced either a decrease or no weight gain in the 3rd coating. This seems to indicate that the coupon surface has reached the saturation point after the 2nd coating and any additional coating of alumina sol does not increase the loading of alumina.

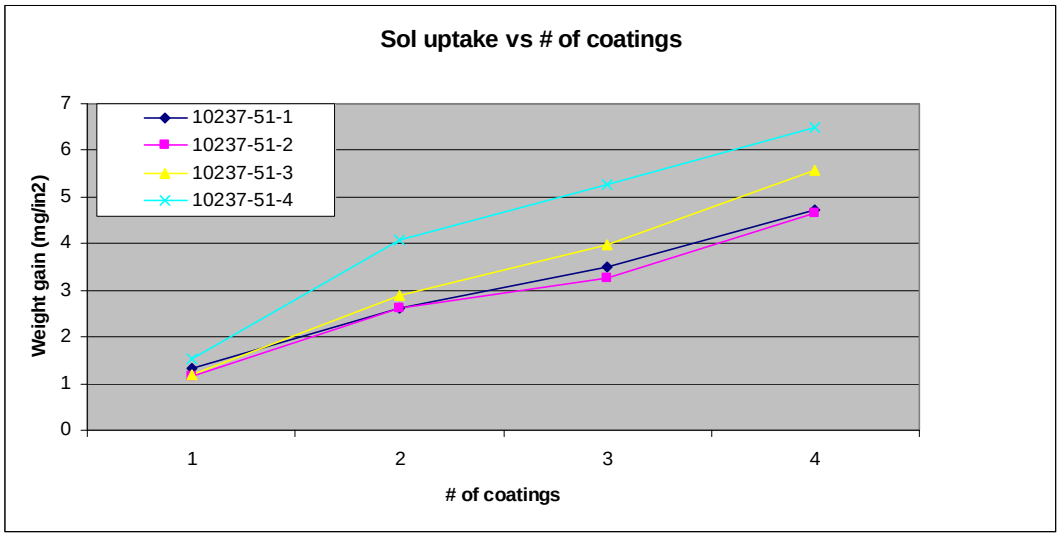

Figure 2: Weight gain vs. number of coatings for alumina sol.

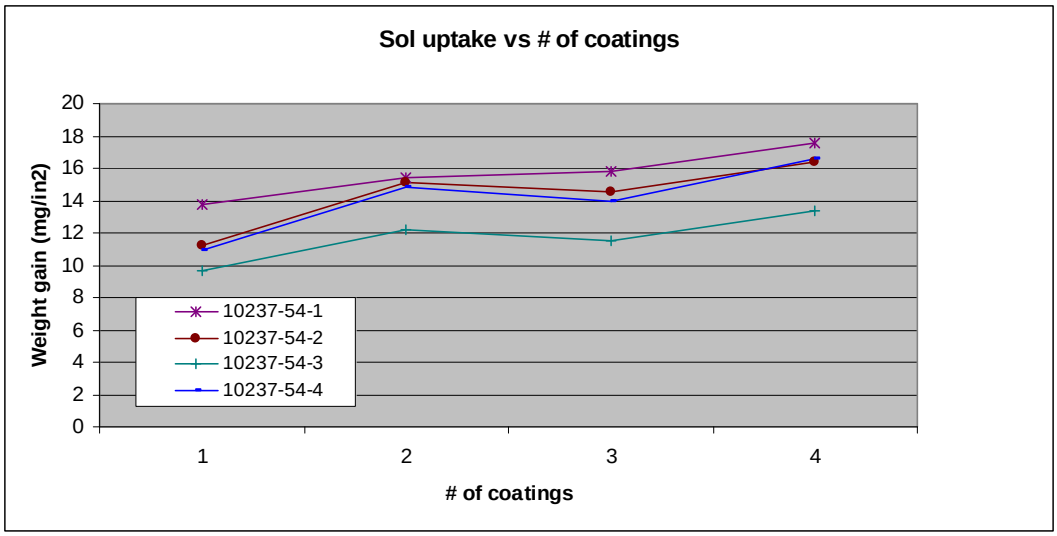

Figure 3: Weight gain vs. number of coatings for additive + alumina sol.

A number of surface pretreatments were investigated and a method was identified that provides a corrosion resistant surface with sufficient chemical and physical stability to avoid catalyst delamination. Figures 4(a-c) are SEM micrographs after a 1000 hour corrosion test at 960^{o}C in a combustion atmosphere. As can be seen, the alumina washcoat applied as an alumina sol is uniform with no observable delamination. The total sol-derived-alumina loading was 2.9 mg/in^{2}.

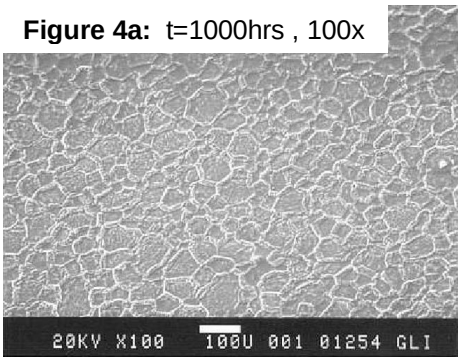

Figure 4a: t=1000hrs , 100x

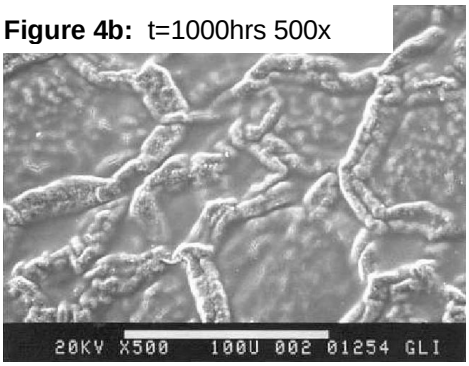

Figure 4b: t=1000hrs 500x

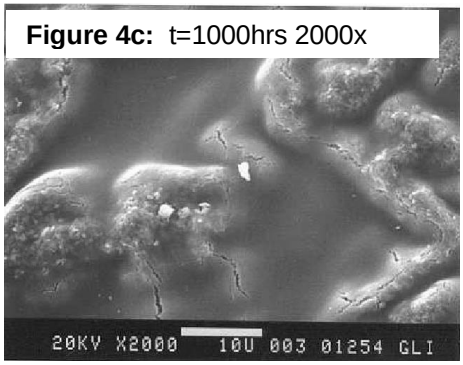

Figure 4c: t=1000hrs 2000x

Figure 4. Surfaces of sol coated, pre-treated alloy coupons after 1000 hrs in a corrosion test with a wet oxidizing atmosphere at 960^{o}C.

With the development of a wall pretreatment step that is resistant to corrosion and which alumina adheres to, three approaches to coating the catalytically active materials on stabilized channel walls are possible. They include washcoating with: 1) an aqueous slurry of the catalyst, 2) an aqueous solution of the catalytic metal salt and 3) a multi-step process involving application of an alumina sol followed by coating with an aqueous solution of the catalytic metal salt. Results for the direct coating of catalytic metals, using metal salt precursors, suggest that the catalytic metal precursor has a significant effect on metal dispersion, as determined by TEM. TPR experiments of alumina- supported platinum bimetallic catalysts reveal a significant effect on the reducibility of the platinum, as illustrated in Figure 5, as compared to a Pt-Cu-Sn catalyst patented by Dow.

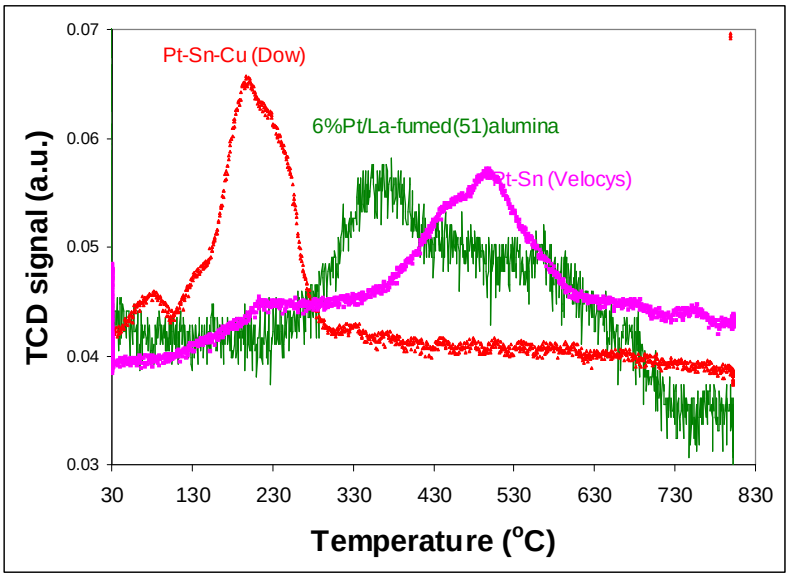

Figure 5: TPR profiles of alumina-supported platinum catalysts

A Pt catalyst supported on an alloy pellet without the oxide coating was tested in a short microchannel reactor. The results of the tests with this catalyst are presented in Figure 6. The results are at least comparable to those reported by Henning and Schmidt [2], who reported selectivity of ethylene of 71% at 55% conversion of ethane with a 2:2:1 ethane:hydrogen:oxygen feed and a Pt coated monolith catalyst.

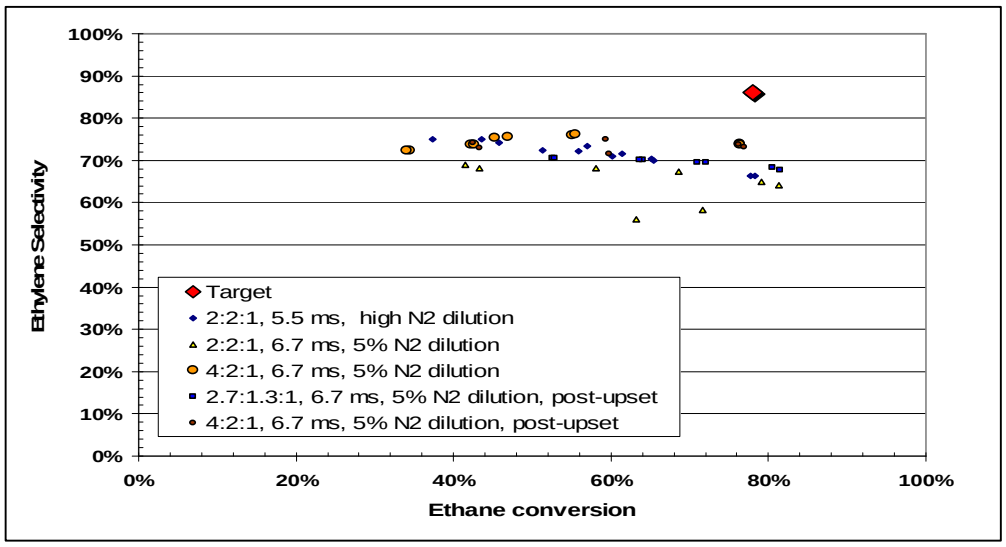

Figure 6. Ethylene selectivities as a function of ethane conversion for a Pt coated coupon tested in a short microchannel reactor.

This result achieveD the milestone for July 2004 to demonstrate catalyst adaptation to the microchannel geometry. The activity and selectivity of the coated Pt catalyst was comparable to the activity and selectivity of a conventional Pt catalyst coated on a monolith.

Velocys developed proprietary catalyst formulations for the OHIO program. Velocys tested these catalysts extensively in microchannel reactor systems. Dow compared two new formulations against an existing formulation in a more conventional adiabatic system to see if they differed in performance.

Three formulations were tested by Dow; one from Dow and two from Velocys, in a special reactor system originally designed for another program that had the feed and analytical capabilities. It is an unusual design with a glass tube surrounded by about three inches of thermal insulation inside of a pressure shell. That arrangement allows for high temperature operation at elevated pressures with minimal heat losses. These studies were performed at 17 psig of pressure, as this is about the lower limit for the current experimental system.

The same sets of conditions were used for the three catalysts tested, designated $Pt/Sn/Al_2O_3$ (The Dow Catalyst), Velocys "A" and Velocys "B". The catalyst volume was 6 cc in each case. Dow also tested the Dow catalyst with 12 cc of catalyst volume. In this reaction system, important variables are flow rate, preheat temperature, pressure, and feed composition. Of particular importance is the overall Fuel to Oxygen ratio or "F/O". High F/O creates a cool reaction condition with low conversion but higher selectivity. As the F/O is decreased, the temperature rises and the conditions are more severe with higher conversion but lower selectivity. Note that temperature is dictated by the preheat temperature, the feed composition, and to some degree the catalyst formulation and is not an independent variable as it is in many catalytic studies.

The results for the three catalysts are shown below in Figures 6, 7 and 8. The system was at about 17 psig for these studies. The flow rate was varied; fuel to oxygen ratio; preheat temperature ("Preheat SP"), and catalyst type in the studies. The ethane to hydrogen ratio was maintained at one. The conversion of ethane is reported as the fraction of the moles of ethane in the feed stream that are not in the product stream. The selectivity reported is to ethylene, ignoring other valuable products such as propylene. The selectivity is the moles of ethylene in the product divided by the number of moles of ethane that were consumed. The main byproducts in order are CO, CH_4, and CO_2. The catalysts performed similarly except that Velocys "A" had a consistently lower conversion than the other two at the same nominal conditions. The Pt/Sn formulation was more selective to ethylene than the other two.

Effect of Varying Fuel / Oxygen Ratio for Test Catalysts

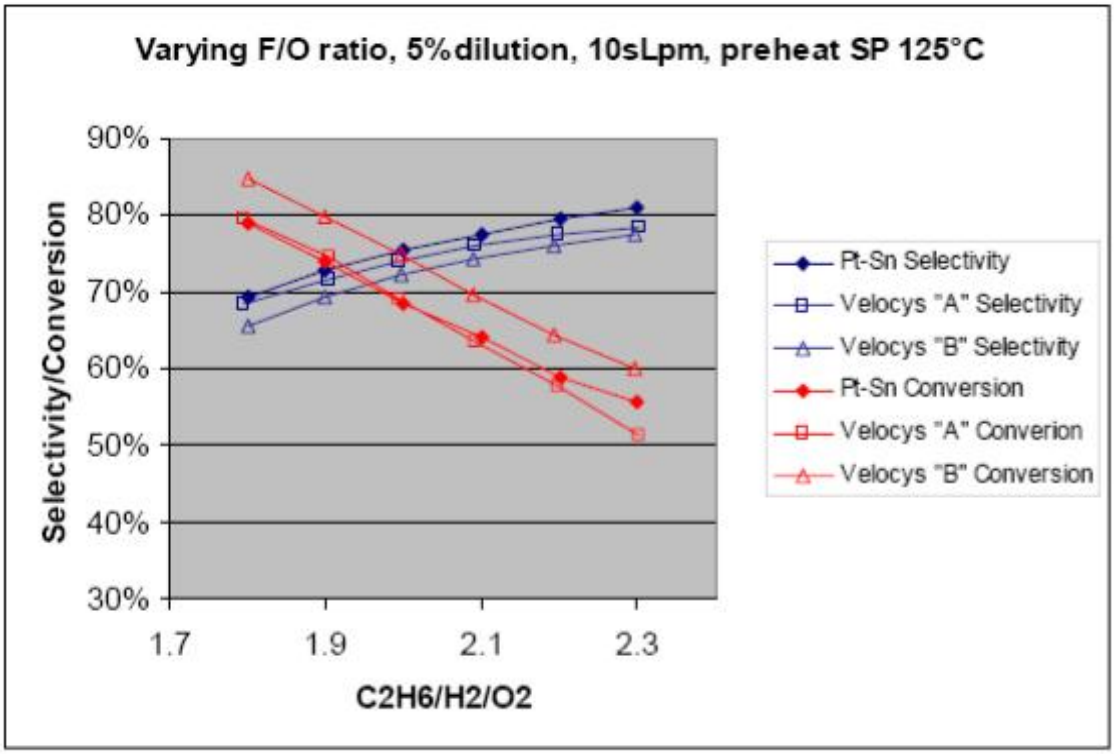

Figure 6. Effect of Varying Fuel/Oxygen Ratio for Test Catalysts.

Selectivity versus Conversion for Test Catalysts under Same Conditions

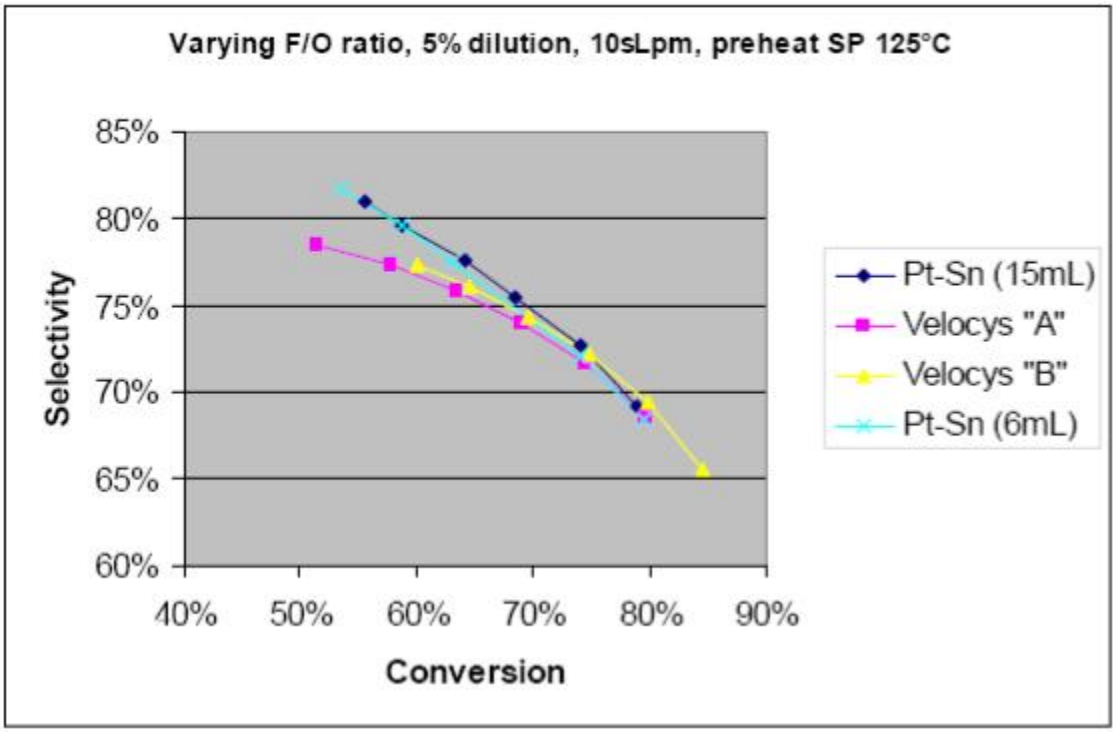

Figure 7. Effect of Varying F/O Ratio on Test Catalysts

Selectivity versus Conversion for Test Catalysts for All Test Conditions

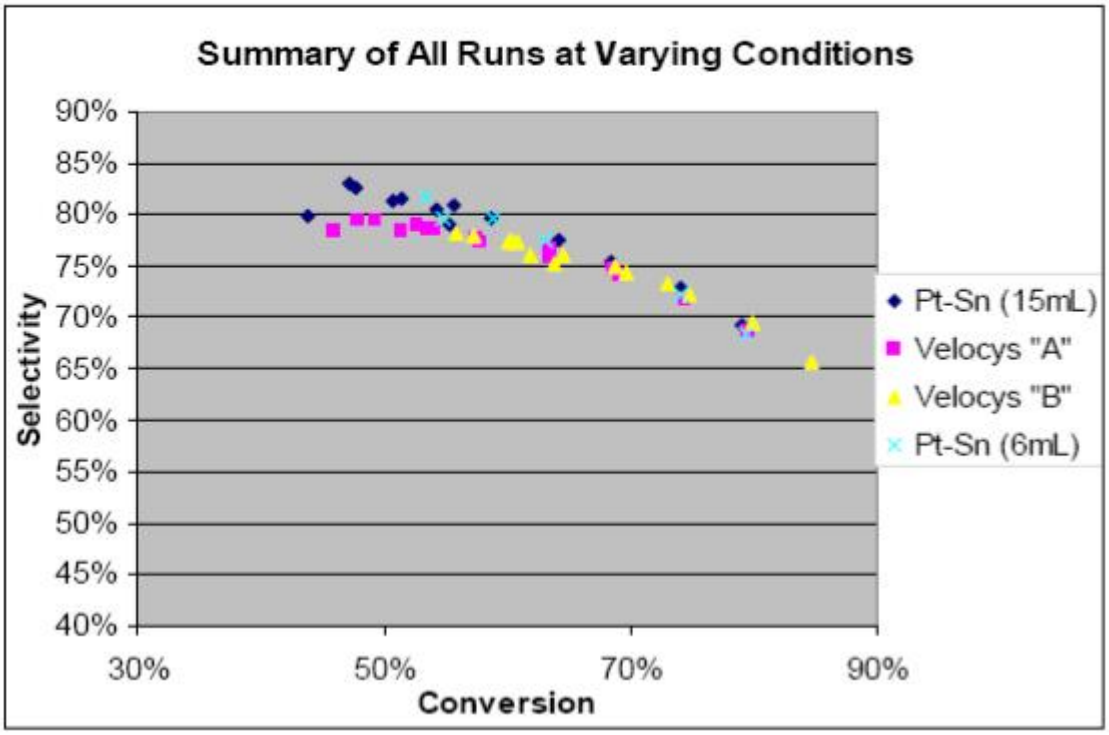

Figure 8. Selectivity vs Conversion for Test Catalysts at All test Conditions

The conclusion from these tests is that the catalysts are not significantly different in terms of selectivity at high conversions. Any improvement in the selectivity at high conversion observed in the microchannel tests can thus be attributed primarily to the reactor design and not to the new Velocys catalyst formulations.

Task 3: Single Channel Model

A simplified 10-step kinetic mechanism was developed to guide reactor sensitivity investigations. The kinetic expressions used in the model were developed by determining the major contributing reactions that described the overall reaction while maintaining an energy balance. The activation energies and pre-exponential factors were determined by fitting CFD model results to experimental findings sited in the literature sources.

The simplified kinetic model was validated by comparing Velocys CFD predictions to reactor model results found in the literature. The kinetics were determined to sufficiently capture the major trends of the experiments. The validation compared both the simplified set of kinetic expressions as well as the detailed kinetic model described by Zerkle *et. al*., J. of Catalysis 196, 18(2000) to the experiment sited by Bodke, A.S. *et. al*., J. Catalysis 179, 138(1998). The geometry modeled was a .25 mm diameter tube that had catalyst applied along 10 mm of length.. The inlet feed consisted of ethane and oxygen only. Figures 9 and 10 show that the simplified

model is adequate for preliminary design purposes since it gives comparable conversions, selectivities, and temperature profiles as the detailed model and the experiments.

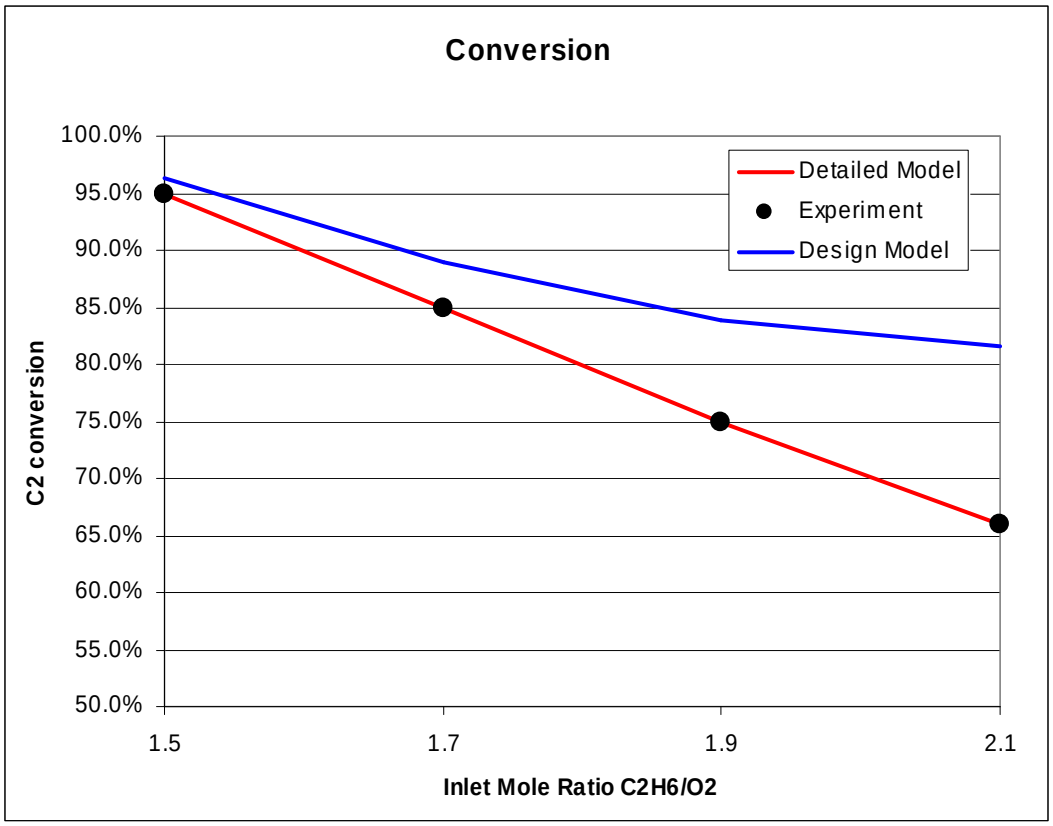

Figure 9. Comparison of simplified kinetic model results to literature detailed model results and experimental results.

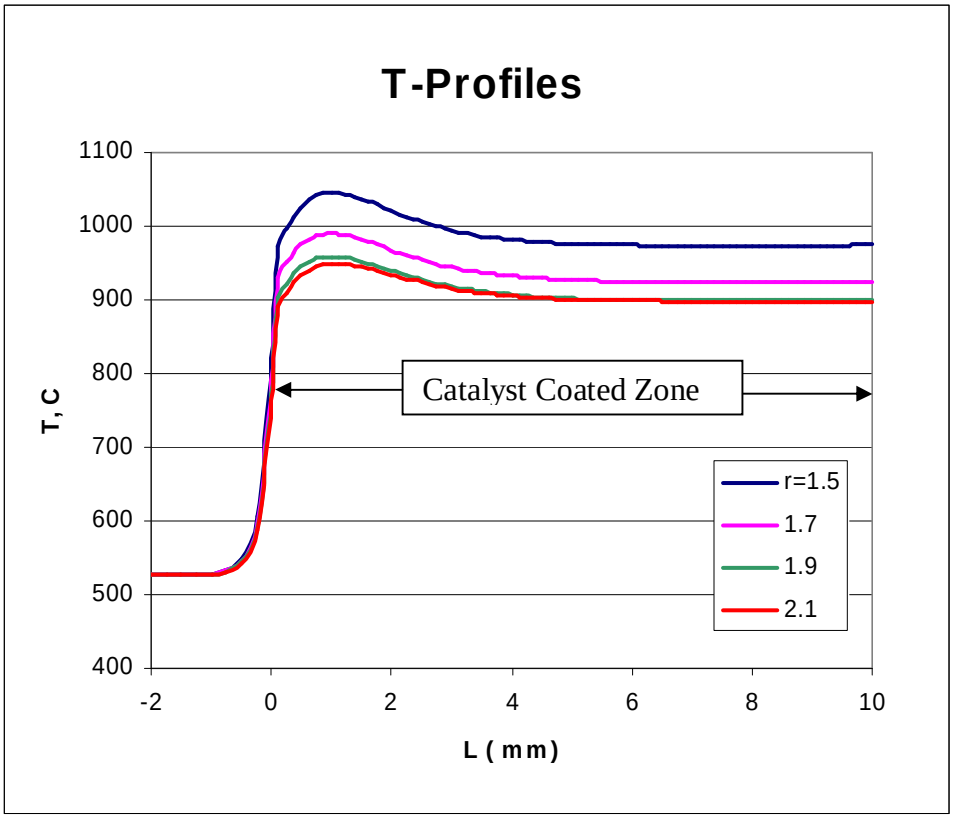

Figure 10. Temperature profiles from the simplified kinetic model ; r = C2H6/O2 Ratio

A simplified kinetic mechanism was modified based on fitting to early results. Heterogeneous steps that were found to be slow were omitted leaving 6 reactions. The activation energies and pre-exponential factors were determined by fitting CFD model results to experimental results. The 6 reactions remaining in the model are:

Homogeneous reactions:

R1. $C_2H_6 + 0.5O_2 \rightarrow C_2H_4 + H_2O$
R2. $H_2 + 0.5O_2 \rightarrow H_2O$
R3. $C_2H_4 + O_2 \rightarrow 2CO + 2H_2$
R4. $C_2H_6 \leftrightarrow C_2H_4 + H_2$
R5. $2\ C_2H_6 \rightarrow 2\ CH_4 + C_2H_4$

Heterogeneous Reaction

R6. $H_2 + 0.5O_2 \rightarrow H_2O$

The model gives good results when compared to experimental data. Figures 11 and 12 show the reconciliation plots for both ethane conversion and ethylene selectivity. The range of conditions used for this analysis are shown in Table 1.

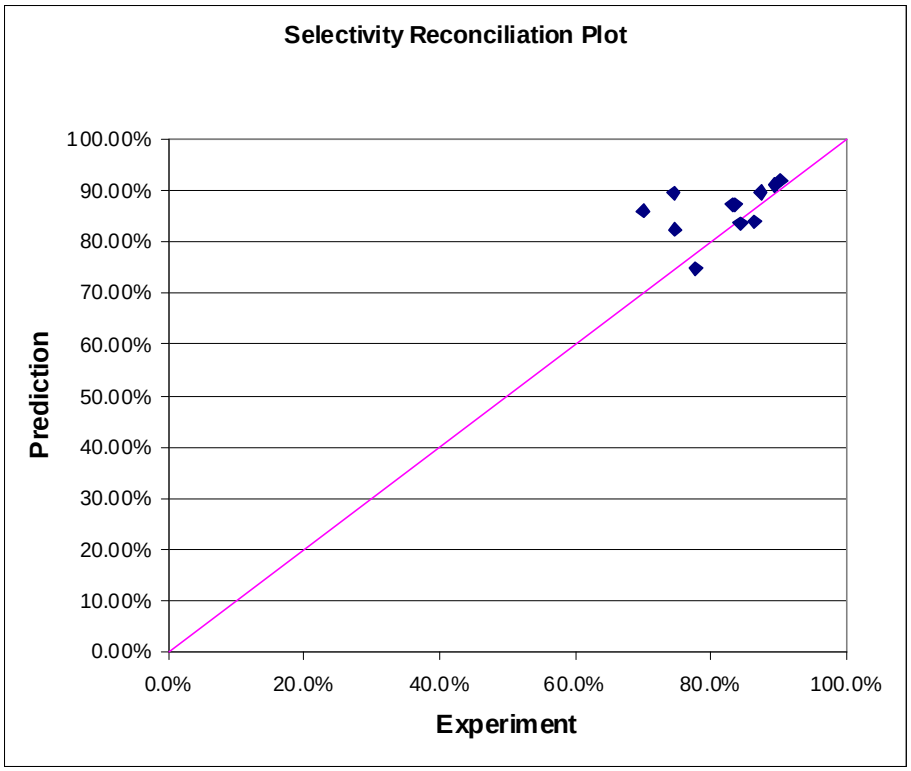

Figure 11: Reconciliation Plot of experimental ethane conversions vs predictions**.**

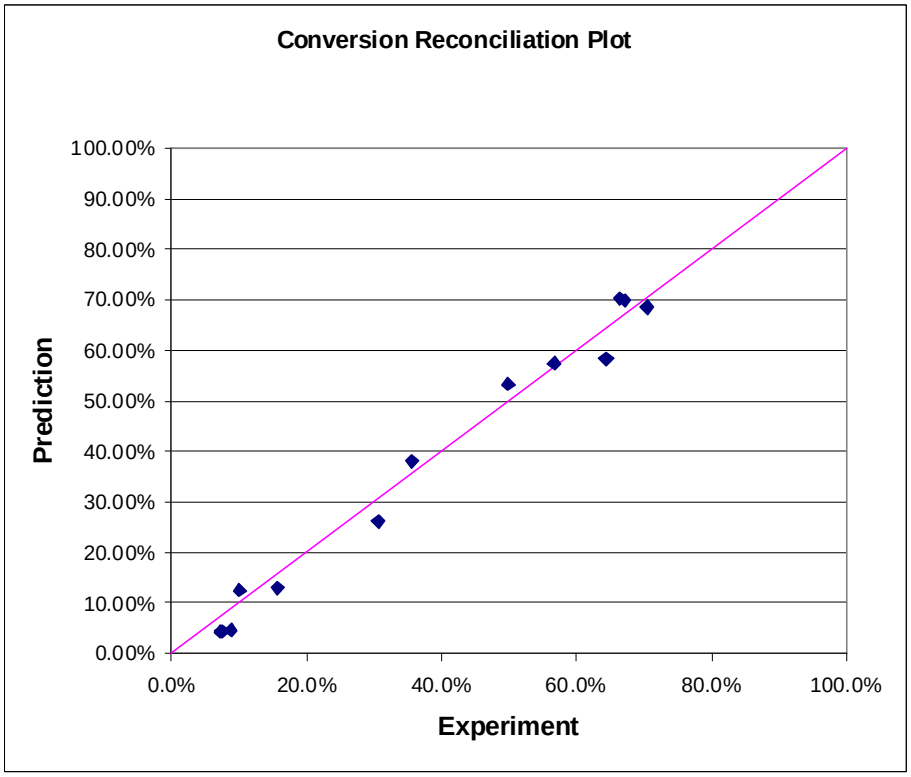

Figure 12: Reconciliation Plot of experimental ethylene selectivity vs predictions

Table 1: Range of experimental inlet conditions used for kinetic model validation.

Inlet Reactor Temperature (ºC)	C2H6:H2:O2 ratio	Contact Time (ms)
800-1000	2:2:1 to 10:2:1	5 to 40

Two reactions have been added to the simple kinetic model to begin building a skeletal network that will permit prediction of coke formation as a function of process variables.

R7 C2H4 -> C2H2 + H2
R8 C2H2 + C2H4 -> C4H6 (butadiene)

The reaction R7 was added to account for the acetylene observed in our kinetics testing. Acetylene is widely accepted as the precursor for coke. The reaction R8 was added to represent the complicated mechanism related to chain growing reactions from acetylene leading to coke. The activation energies and pre-exponential factors for each reaction were determined by fitting CFD model results to experimental results. In particular, low ethane conversion data was used in fitting the parameters in the reaction rate expression of R6, since under those conditions no coke formation was observed in the experiments. The carbon loss data observed under the conditions leading to high ethane conversion rates was used in fitting the parameters in the rate expressions for reaction R7.

A CFD model was built of the microchannel reactor. This reactor comprised a short microchannel zone (approx 4 cm long) with a narrow cross section (0.040 inch x 0.5 inch), held between two sections of 0.5 inch OD tubing. The model accounts for the effect of a furnace placed around the reactor.

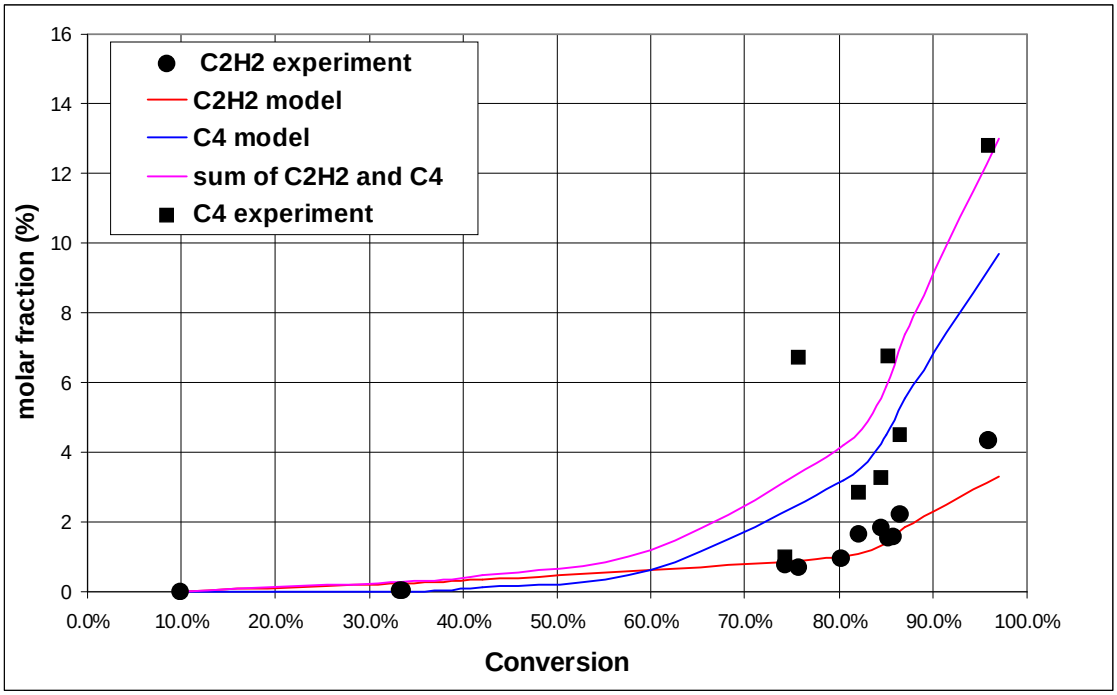

Figure 13. Comparison of the calculated C2H2 concentration from a simplified kinetic model to experimental results with a microchannel reactor.

The model predictions of acetylene concentration are plotted in Figure 13 together with the experimental data. The solid lines are the model results. Over the whole range of ethane conversion rates the model predicted acetylene contents in the product effluent (solid read line) is in good agreement with the testing data.

Task 4 – Operate Single Channel Reactor

The Mod 2 reactor was operated under a number of different test conditions. The catalyst activity was much lower than anticipated, possibly due to an early upset during testing, and the performance at the 3:2:1 ethane to hydrogen to oxygen design ratio was only ~78% ethylene selectivity at the 78% ethane conversion target. An interesting finding however, was that the selectivity to ethylene could be increased by lowering the oxygen concentration in the feed. This lead to a test using a 6:2:1 ratio that achieved near target performance of 84% ethylene at 77% ethane conversion. Under these conditions however the reactor depended on external heat to run at steady state.

Further tests were performed using straight steam cracking conditions, with only ethane and H_2O in the feed, and these tests showed very encouraging results of 91% ethylene selectivity at 62% ethane conversion and 86% ethylene selectivity at 78% ethane conversion. Figure 14 summarizes the conversion vs selectivities for all conditions run.

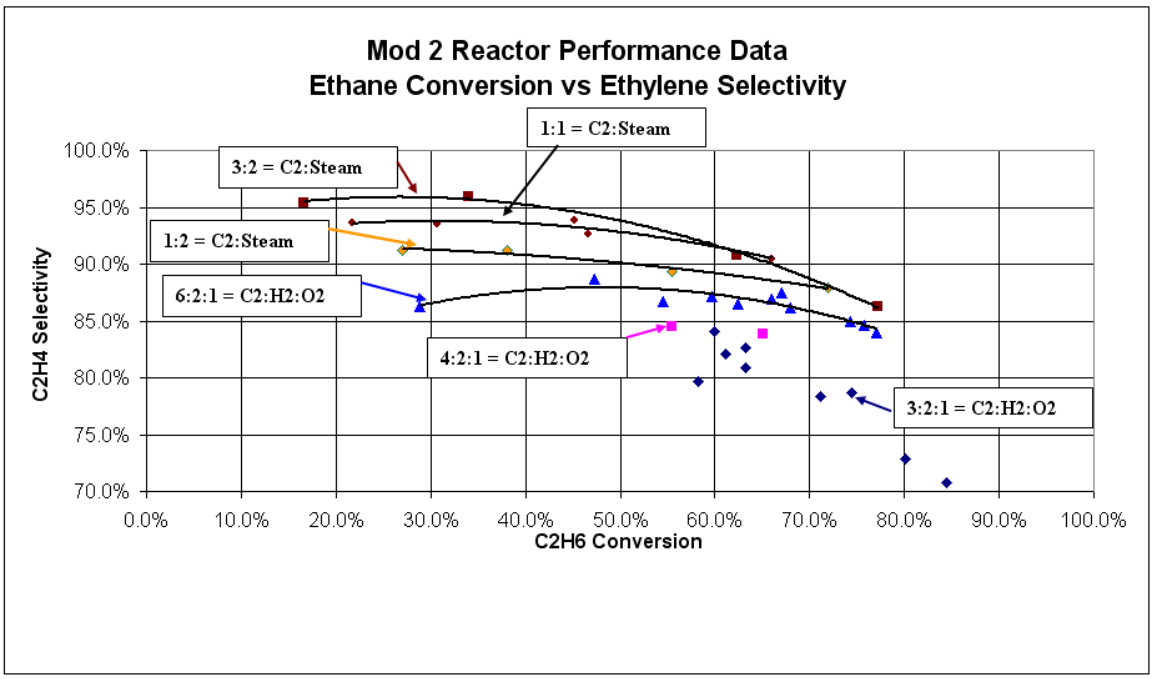

Figure 14: Mod 2 Reactor Experimental Data Set

Under all conditions run however, the Mod 2 reactor experienced steady pressure drop increases. The Mod 2 reactor was taken offline and had the catalyst coated inserts removed and analyzed.

The reactor showed fairly heavy deposits of carbon in the reactor section of the device. The carbon was mostly concentrated in the small finned channels of the catalyst coated insert. SEM analysis showed that very little Pt and practically no Sn remained on the insert.

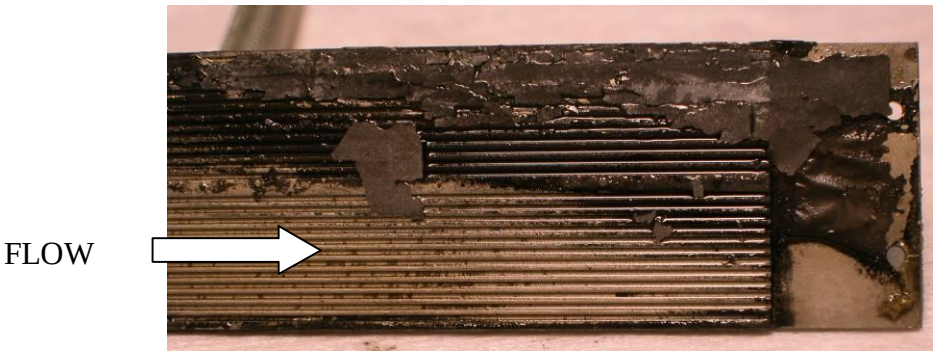

Figure 15: Significant Carbon Deposited on Insert

Computational fluid simulations were run to examine the role of fluid flow in the carbon deposition. The results showed that there were significant stagnant zones and recirculation zones set up in the flow field just at the exit of the catalyst coated finned channels located on the inserts. This is a strong indication that the very poor mixing in these zones contributed to coke formation. As carbon was deposited in this zone the flow field would be further affected that would act to compound the problem and eventually lead to blockage of the finned channels themselves.

This analysis lead to a redesign of the catalyst coated insert in order to remove all significant recirculation zones in the flow field. The Mod 2 high capacity reactor was modified in order to mitigate carbon build up during the initial testing of the reactor. Computational fluid dynamic simulations were used to identify coke-prone regions that correlated well with carbon deposits found within the device after the initial testing. Several device modifications were made, including altering the catalyst support geometry and the transition between the oxidation and cracking zones of the reactor. The Mod 2 reactor then had catalyst reapplied and was restarted. The catalyst used for this series of test was a reactively coated Pt solution that was not expected to get as favorable ethylene selectivity results as the previously used Pt-Sn catalyst but was expected to have a longer operational life and therefore could be used for a series of case studies.

The reactor modifications resulted in a dramatic improvement on prolonging the amount of time on stream without requiring any carbon burnout steps.

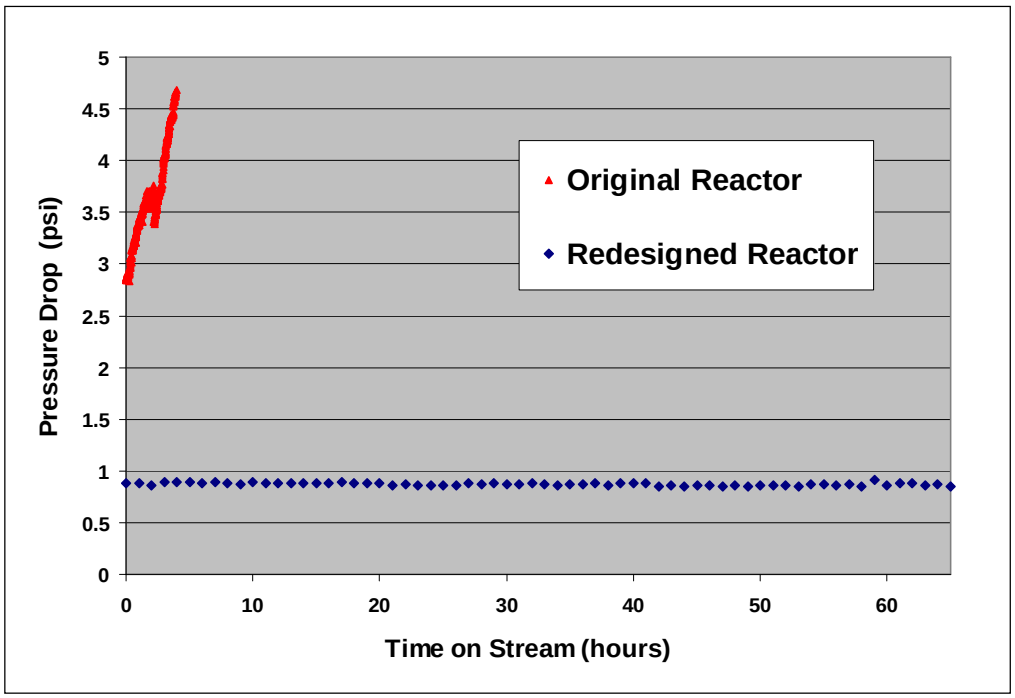

Figure 16: Pressure drop for original design and redesigned Mod 2 reactors during ethylene production tests.

The Mod 2 reactor was then used to study the effects of several operational parameters on reactor performance. Specifically the effects of C2:O2 ratio, H2 concentration, and flowrate, were all studied.

Sensitivity to C2:O2 ratio: In general, reducing the oxygen concentration in the feed has a positive impact on C2H4 selectivity. This is clearly shown on the following Figure.

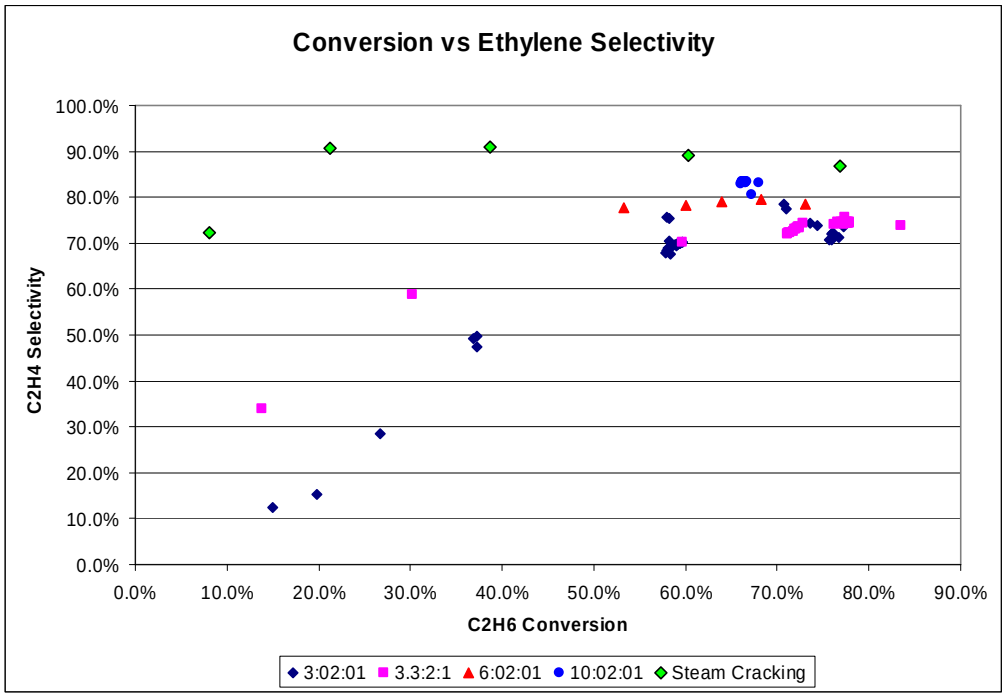

Figure 17: Mod 2 experimental results showing the effect of C2:O2 ratio on performance.

Sensitivity to H2 concentration: Most experiments have been run at a 2:1 H2:O2 ratio. The Mod 2 was used to explore modifying this ratio and selectivity improvements were noted with increasing hydrogen to oxygen ratio

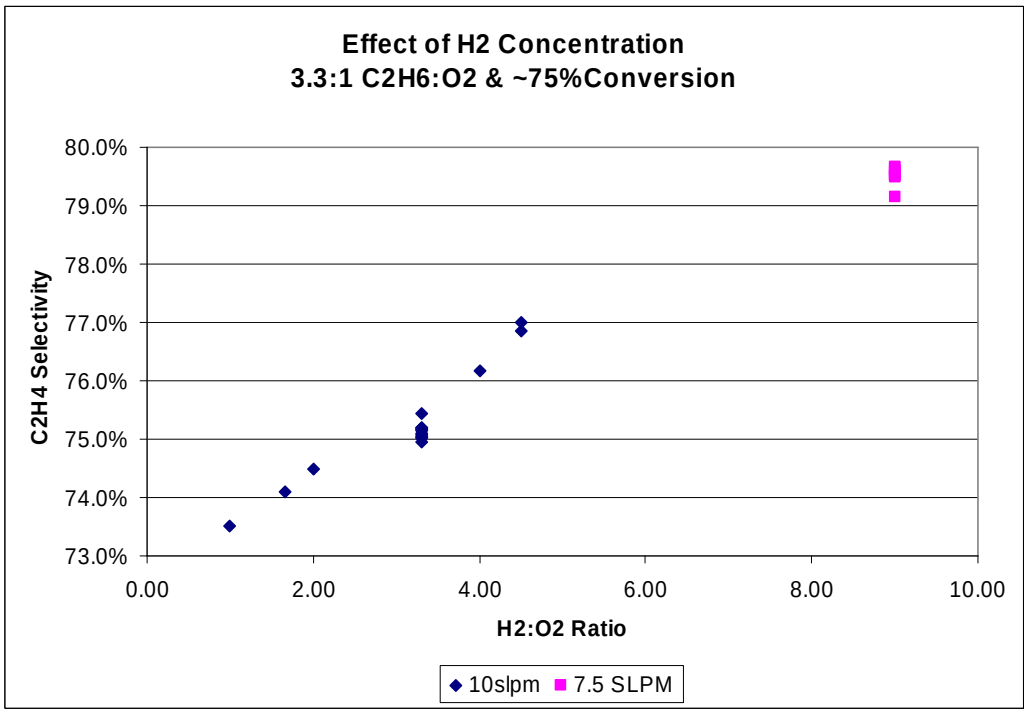

Figure 18: Mod 2 experimental results showing the effect of H2:O2 ratio on performance.

Sensitivity to total flowrate: Reducing the flowrate had increased the C2H4 selectivity and yield.

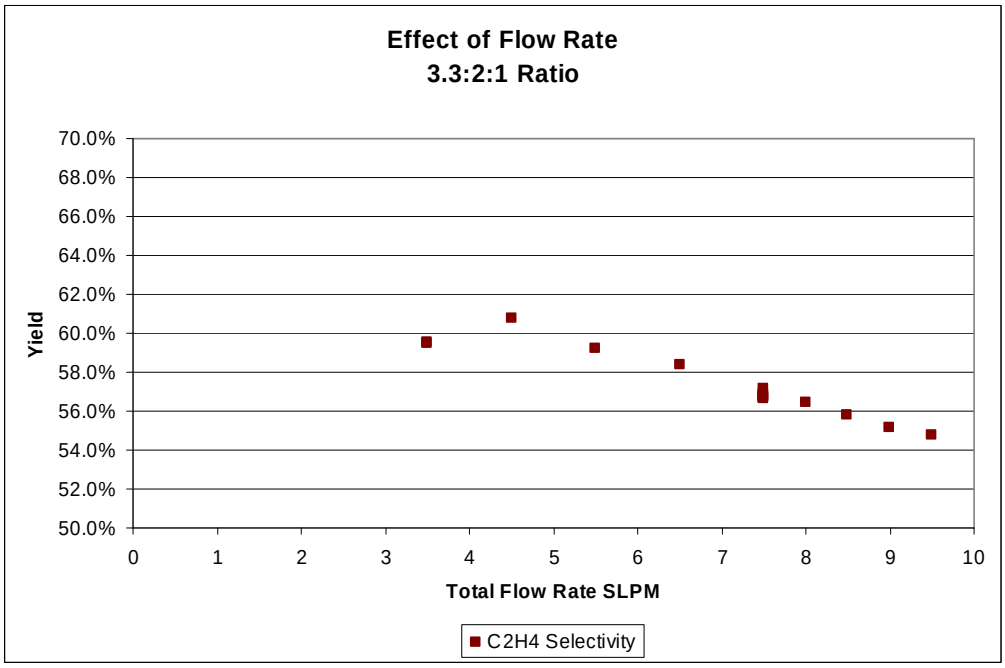

Figure 19: Mod 2 experimental results showing the effect of flowrate on performance.

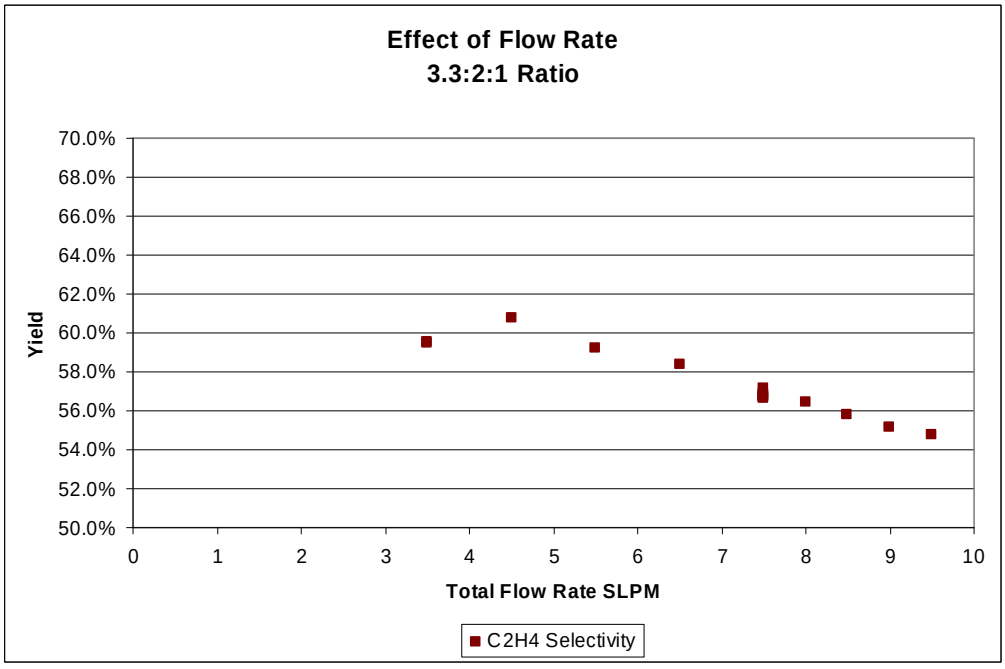

Figure 19: Mod 2 experimental results showing the effect of flowrate on performance.

The revised Mod 2 high capacity reactor coupled with the new catalyst was operated for more than 120 hours at high ethane conversion and high ethylene selectivity before a system upset.. During operation, the pressure drop remained steady at less than 4 psi, as shown in Figure 20. The device was operated at a 4:6:1 ethane to hydrogen to oxygen ratio with a total flow rate of

10SLPM. During the operating window, the ethane conversion exceeded 75% and the ethylene selectivity exceeded 82%.

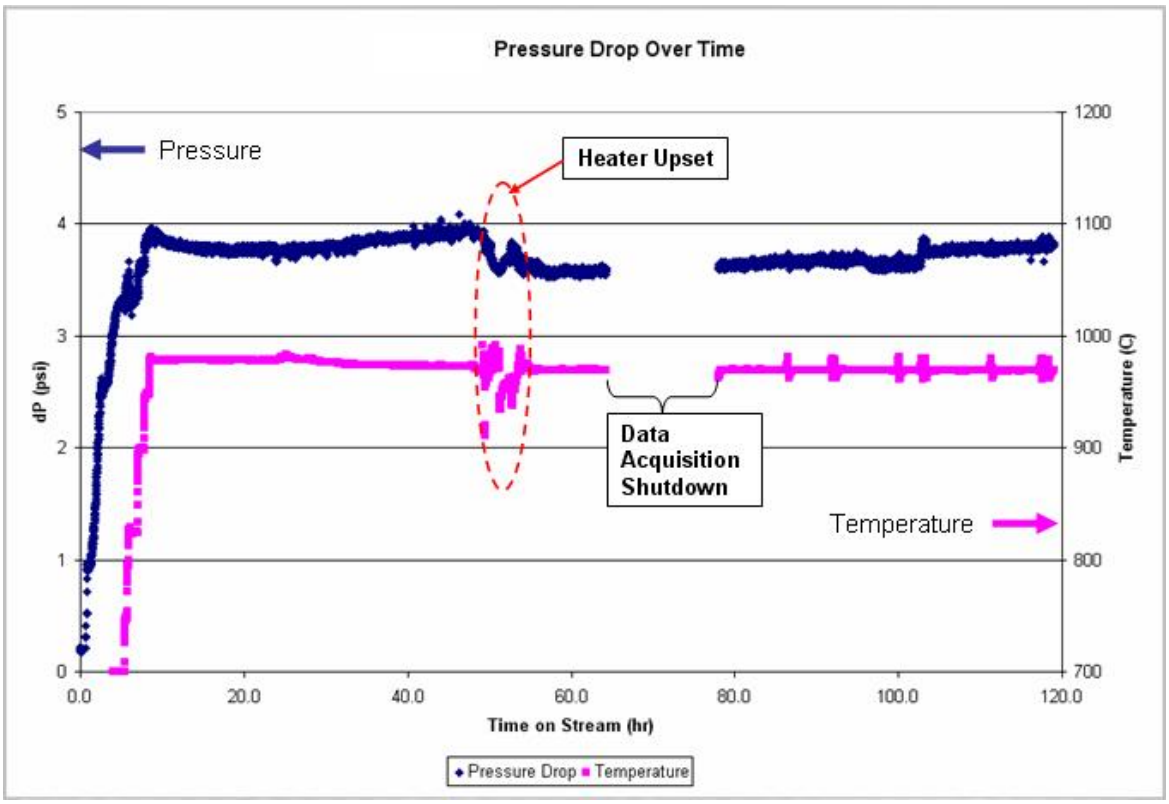

Figure 20. Mod 2 high capacity reactor showing steady pressure drop over 120 hours of operation.

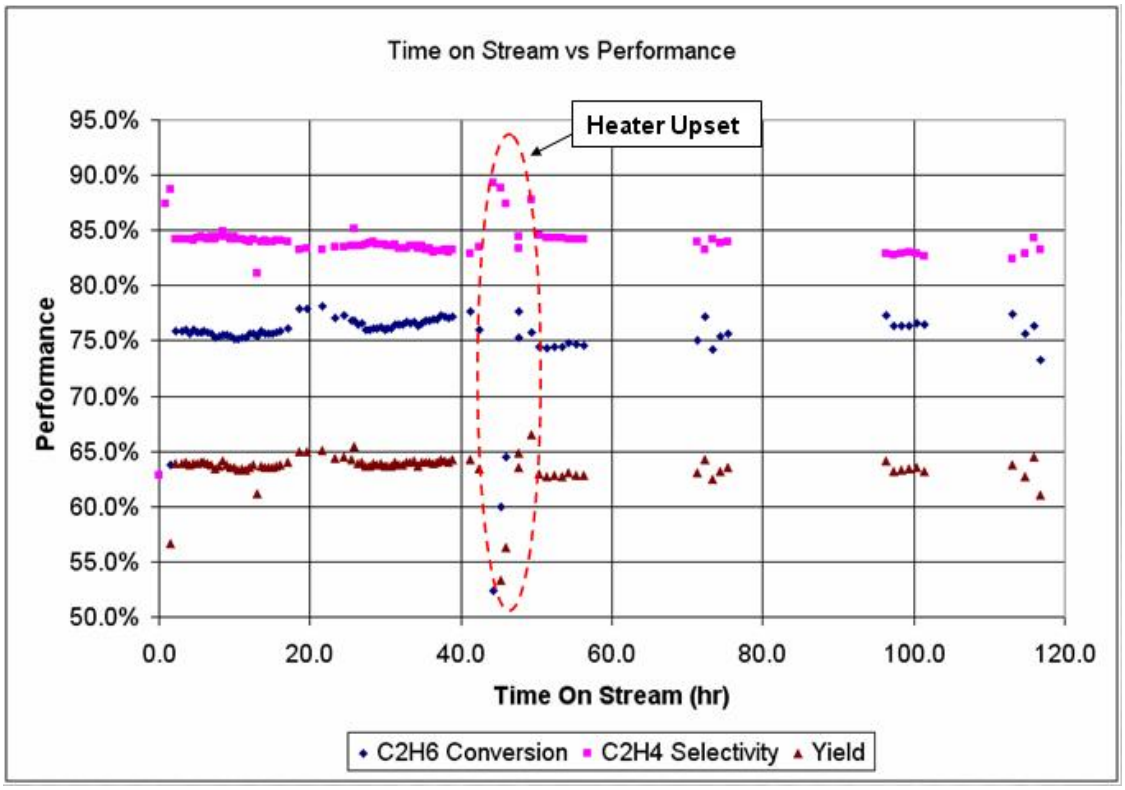

Figure 21. Mod 2 high capacity reactor showing a steady and high yield over 120 hours of continuous testing

The Mod 2 single channel reactor was retrofitted to include a new catalyst formulation. This particular formulation showed more stability than previous catalyst when tested in one of the small reactors while maintaining performance levels that approached the high ethane conversion and high ethylene selectivity catalysts that were demonstrated in the small reactors.

The device was operated at a 4:8:1 ethane to hydrogen to oxygen ratio with a total flow rate of 10 SLPM. While operating under these conditions, the ethane conversion exceeded 75% and the ethylene selectivity exceeded 82%. Although the catalyst performed well, the reactor showed signs of increasing pressure drop early on in the testing. The reactor was de-coked after ~30hrs at target conditions. It should be noted that a similar catalyst formulation also showed a higher tendency for coke formation in one of the small reactors.

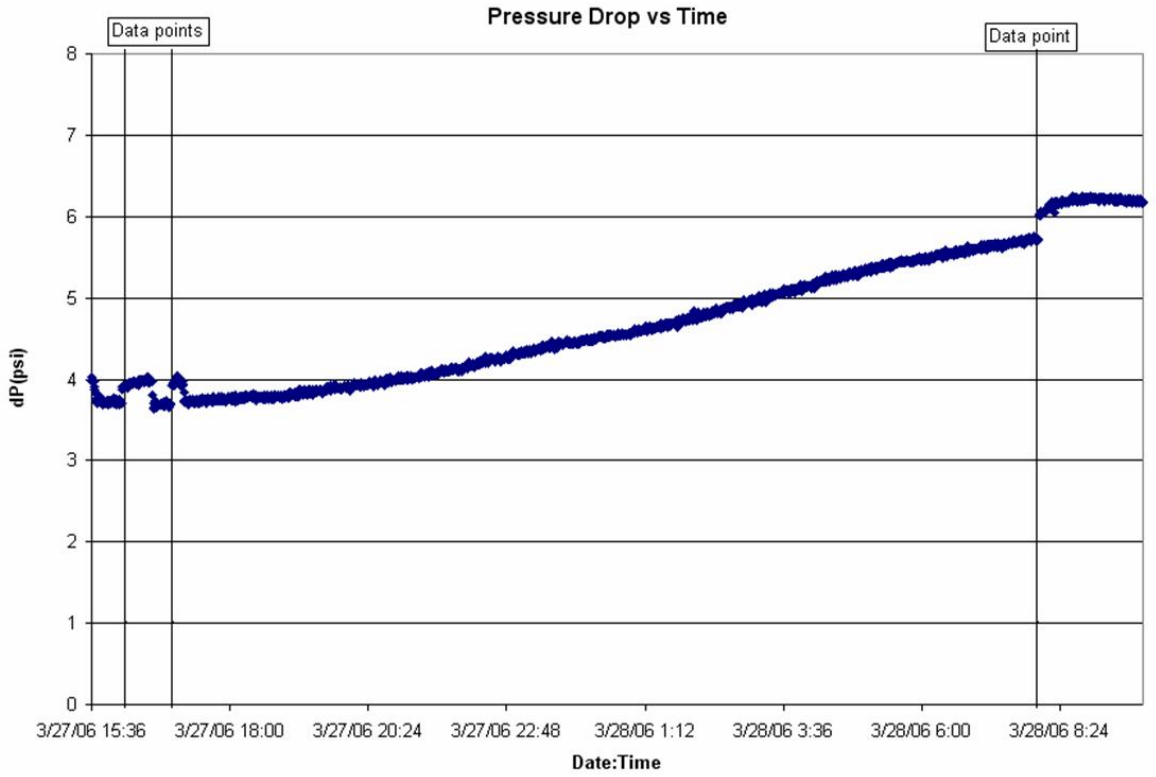

Figure 22. Mod 2 single channel reactor showing increasing pressure drop over a 16 hour period.

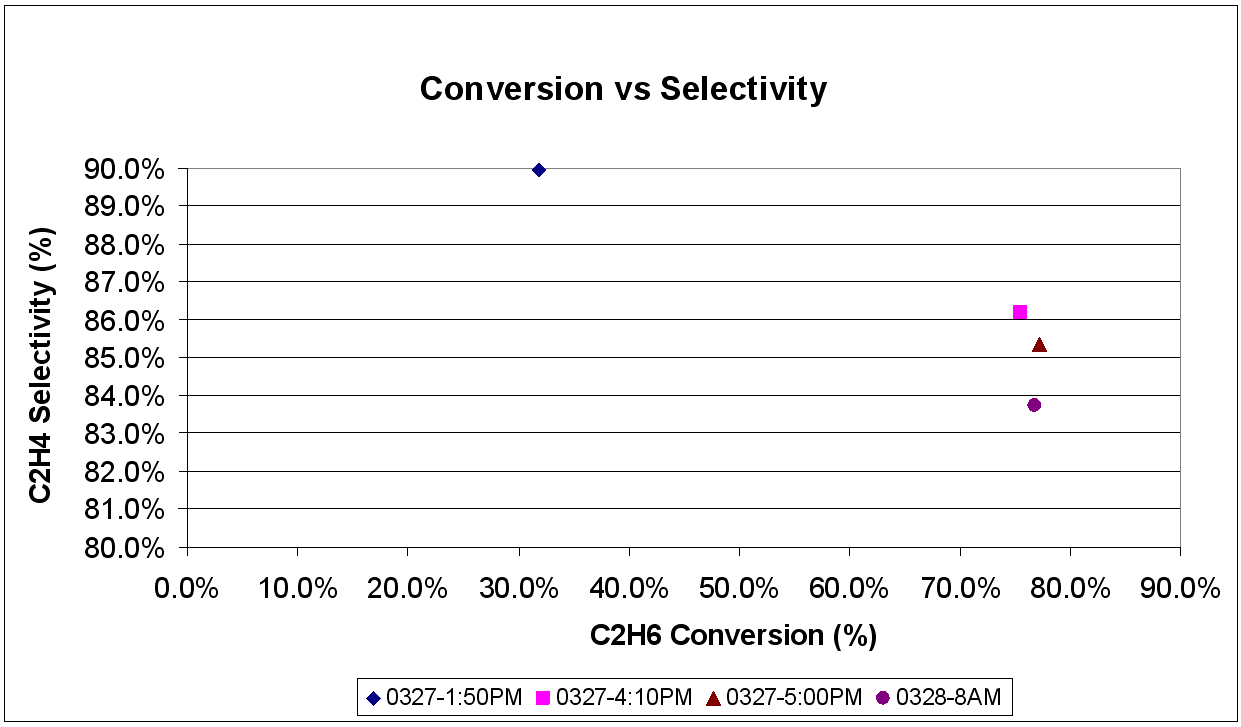

Figure 23. Mod 2 single channel reactor showing conversion and selectivity over ~ 20 hrs of operation

Task 6 – Catalyst Stabilization

New catalyst compositions, V1 and V2, were prepared, with the expectation they would exhibit better stability than Pt-Cu under reaction conditions. Coupons with V1 coated on the surface also exhibited good performance. Furthermore, the V1 and V2 catalysts were stable. The performance did not change over a 100-hour time on stream period. The pressure drop was less than 0.34 psi during the tests. After testing, the catalyst weight loss was only 8%, indicating good adhesion and little if any vaporization.

For V2 coated coupons, the maximum ethylene selectivity was 83% at 77% ethane conversion, which is close to the performance of Pt-Cu catalysts. After testing, some coke was found at the catalyst surface. Testing of modified V1 and V2 catalysts is in progress.

Three Pt-Cu coated coupons were characterized by surface XRD, SEM/EDS and XPS analyses. Surface XRD and SEM/EDS can provide information within a few microns from the surface. XPS can detect surface within several atomic layers. One coupon was coated with Pt and then Cu at room temperature. The second coupon was heat treated at 900 ^{o}C for 4 hours in flowing H_2 after the Pt-Cu coating. The third coupon was calcined at 900 ^{o}C for 4 hours in air after the H_2 heat treatment. For the fresh Pt-Cu coated coupon, only Pt and Cu metal phases were seen (XRD profile in Fig. 26). The surface was fully covered with nano-size Cu metal particles (TEM and XPS). After the heat-treatment in H_2, the Pt and Cu particles sintered (SEM) and formed a Pt-Cu solid solution and Cu_3Pt alloy (SEM and XRD in Fig. 26). Both Pt (18 mol%) and Cu (82 mol%) were seen at the surface (XPS), suggesting Pt and Cu inter-diffusion at high temperatures. After calcination in air, Cu was oxidized to CuO (XPS). The surface was covered with micron-size CuO (XRD, SEM and XPS), while the Pt was still in metallic form underneath.

Based on the above characterization results, it is concluded that CuO is present at the surface in the front of Pt-Cu catalyst bed, where O_2 is present. With O_2 consumption, the second zone is changed to a reducing atmosphere, where the Cu_3Pt alloy is present.

Table 2. Summary of catalyst testing results

Catalyst	Synthesis method	T inlet (°C)	X (C_2H_6) (%)	S (C_2H_4) (%)	S (C_2H_2) (%)	C-loss (%)
1. Pt-Cu (1:3.3)/doped NiAl (20.8 mg/in^2)	reactive coating	920	79	83	2	4
2. Pt-Cu(1:3.3)/doped NiAl (23 mg/in^2)	reactive coating	905	79	82	4	4
3. V1 (0.6:1)/NiAl (13 mg/in^2)	reactive coating	885	77	80	2	0
4. V1 (2:1)/NiAl (12.5 mg/in2)	reactive coating	915	79	82	3	4
5. V1 (5:1)/NiAl (13.4 mg/in2)	reactive coating	948	77	82	4	-2
6. V2 (5:1)/NiAl (13 mg/in2)	reactive coating	900	78	79	2	2
7. V2 (1:1)/NiAl (12.5 mg/in2)	reactive coating	930	77	83	4	3
8. V2 (1:4)/NiAl (12 mg/in2)	reactive coating	907	79	79	3	1

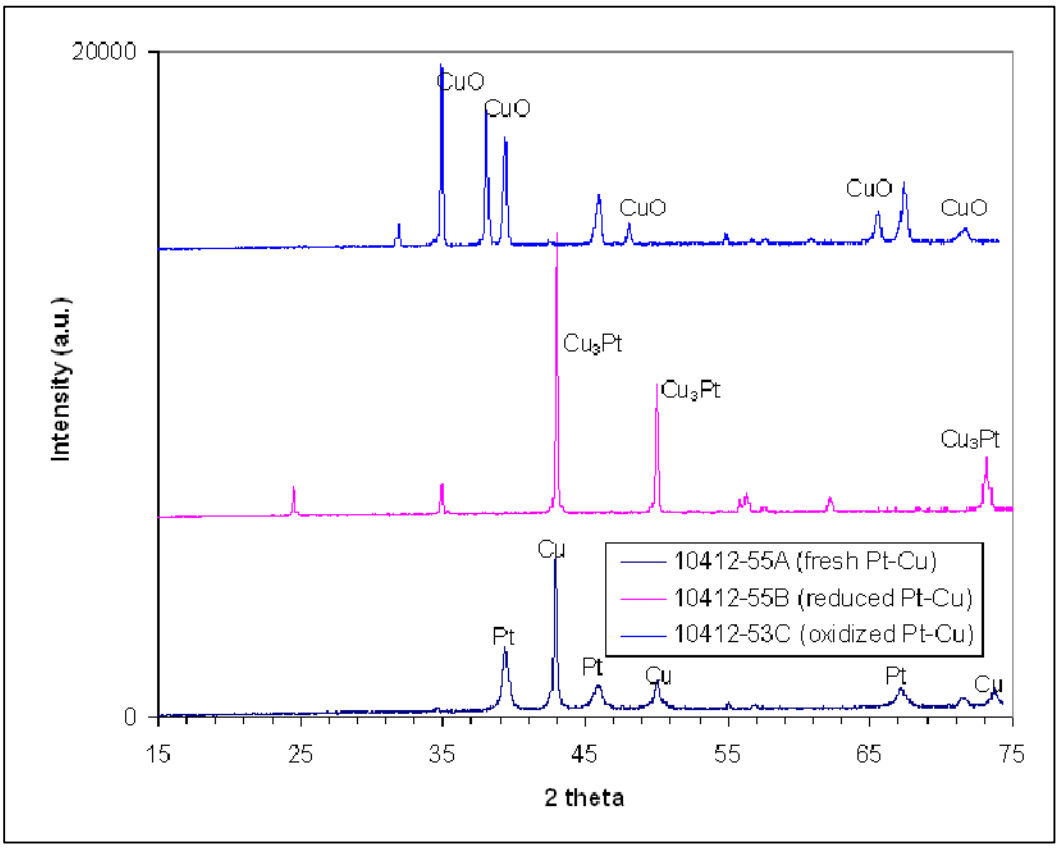

Figure 24. Surface XRD analysis of Pt-Cu coated coupons

One V1-type and four V2-type catalysts were tested in a single channel test reactor (Table 1). The catalysts were synthesized by reactive coating. Reactive coating has the potential to provide a more uniform catalyst coating and reduce coating time versus solution washcoating.

The single channel test reactor has two microchannels separated by a catalyst coupon. Reactants were fed at 3:2:1 ratio of ethane : hydrogen : oxygen. Catalyst entrance temperature ranged from 850 to 950^{o}C, and contact time was fixed at 40 ms. Reaction products, e.g., CO, CO_2, and C1-C4 hydrocarbons, were analyzed with an on-line four-column GC.

As summarized in Table 3, the V1-A catalyst exhibits good ODH activity. Initial ethane conversion (78%) and ethylene selectivity (84%) have met the performance target. However, this catalyst is not stable. After 25-hour on stream, ethylene selectivity dropped to 81%. Also pressure drop was increased from 0.3 to 0.7 psi.

For V2-type catalysts, the metals have lower metal vapor pressures at high temperatures inV1-type catalysts, so these catalysts are expected to exhibit better stability for the oxidation reaction. When V2-type catalysts were coated on Ni-aluminide coupons, they exhibited various activities. The best performance was obtained on the catalyst V2-B (Table 4). Its ethylene selectivity (83%) is very close to that of earlier best catalysts. After 72-hour on stream, 83% ethane conversion and 80% ethylene selectivity were still achieved. The pressure drop was increased from 0.2 to 14 psi, indicating coke formation. Some flakes were seen at the front of the coupon after decoking.

The used V2-B catalyst was analyzed with SEM/EDS. It is noted that the EDS is not capable of separating all of the metal peaks. As seen in Figure 27, most of the surface is covered with catalyst. Sintered metal and some pores with exposed Al_2O_3 are seen on the whole coupon. Some impurities, e.g., Cr and Co, are also detected. Because the testing device was aluminized and heat-treated prior to testing, the coupon should have been chromium free. It is likely the Cr impurity was from the inserted thermocouple, whose surface is covered with Cr_2O_3. It has been demonstrated that the Cr is a poison to Pt for combustion.

Table 3. Summary of catalyst testing results

Catalyst	Synthesis method	T inlet (^{o}C)	X (C_2H_6) (%)	S (C_2H_4) (%)	S (C_2H_2) (%)	C-loss (%)
1. V1-A (17.2 mg/in^2)	reactive coating	935	78	84	4	3
2. V2-A (12.2 mg/in^2)	reactive coating	841	80	80	3	1
3. V2-B(14.9 mg/in^2)	reactive coating	928	78	83	4	-1
4. V2-C (10.7 mg/in^2)	reactive coating	875	78	77	0	2
5. V2-D /(22.7 mg/in^2)	reactive coating	875	77	76	2	-3

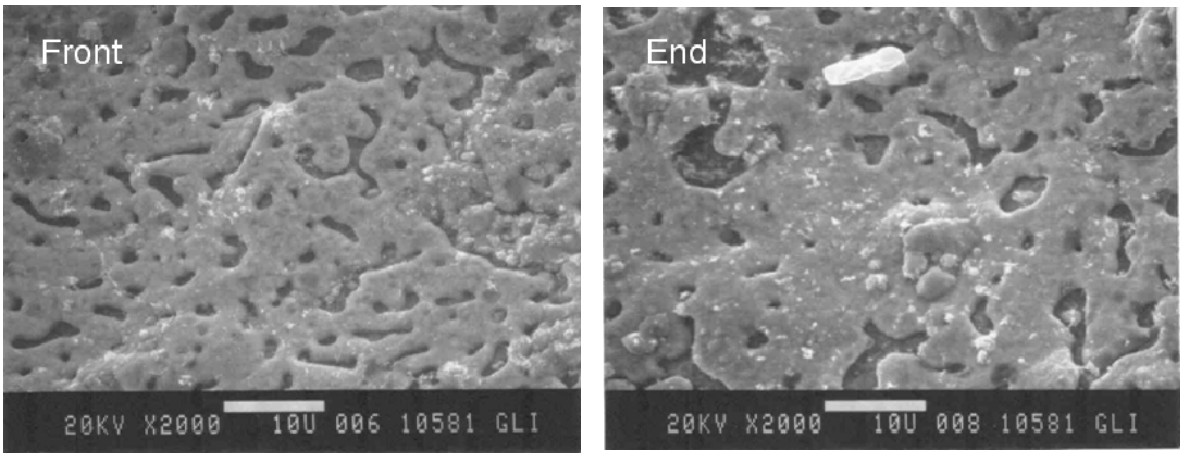

Figure 25. SEM of used V2-B catalyst.

PNNL completed SEM evaluation of several fresh and used catalysts. One catalyst was prepared by Dow using conventional impregnation techniques and a conventional formulation on an alumina monolith. The other two catalysts were prepared at Velocys by reactive deposition of the desired metals on crushed alumina monoliths.

All three catalysts, with Pt and various promoter elements, were tested as reported above. The process tests were conducted in Dow's packed bed reactor. Conversion and selectivity for the three catalysts showed similar selectivity vs conversion profiles under these conventional fixed bed testing conditions. By comparison, in Velocys microchannel reactors the performance of all of the catalysts was better than in the fixed bed reactors.

The used conventional catalyst, Pt/Sn/Al2O3, showed widely dispersed regions covered with small metal particles, on the order of 1 micron in diameter. These particles were depleted in Sn compared to the initial formulation, likely due to Sn evaporation during testing.

Two catalysts with Velocys formulations deposited by chemical reaction were evaluated. These two catalysts were tested in the same manner as the Dow catalyst. Both fresh and used samples were analyzed to evaluate the catalyst evolution after testing.

Examination of fresh Velocys catalysts showed that the various metals were deposited in a decidedly non-uniform manner. Overall the metal loading matched the desired level for each metal. In the analysis there were found regions of each of the metals individually, regions where mixtures of metals were found, and regions which were not coated. The coated regions appeared as thin films overlaying the alumina support. Film regions were hundreds of microns wide but had significant gaps.

Samples of the used catalysts were analyzed by SEM as well. In the used samples, thin films of the metals were better mixed, and there was evidence of both alloying and sintering. The compositions spanned a narrow range. It could not be positively determined whether metal had been lost during the testing although the metal composition was near the fresh composition.

Evaluation of the multi-channel reactor indicates that although the catalyst activity is relatively stable, there are substantial losses of Pt from the surface during operation at ~1000 C. Several mechanisms are being considered for the metal loss, including delamination of the metal film and volatilization. A study of the Pt volatilization was conducted including alloys with metals that may help reduce the Pt vapor pressure.

Task 7 – Optimize Reactor Design and Reconcile Model

The successful modeling of the short microchannel reactors permits the model to be used to explore the window of operating conditions to minimize the coke formation.

The validated kinetics model was applied to the proposed test reactor design. The model domain is a slice of the whole reactor, including one flow channel formed by fin insert, U-bend and the cracking channel. The device perimeter wall temperature is imposed as constant in the reactor section, while in the heat exchanger section, the wall is kept as thermally isolated without thermal loss. In order to study the sensitivity of the reactor performance and the coke formation to the operating parameters, twelve sets of conditions were selected around the design point at which the performance targets are met. Along with the reactor performance predictions of ethane conversion and ethylene selectivity, the level of coke formation in the system is also modeled as well as other by-products. The model predictions of the reactor performance for all the cases are summarized in the following table.

Table 4. Model predictions for Mod 2 device performance.

Run	metal temp	total flow	C2:O2 ratio	C2H6 conversion	C2H4 selectivity	C, selectivity
	C	SLPM		%	%	%
1	1035	7.88	3.71	95.0	69.6	3.7
2	1000	10.00	3.00	83.0	84.1	1.3
3	964	12.12	3.71	63.1	91.5	0.3
4	1035	12.12	2.29	90.7	73.7	2.8
5	964	7.88	2.29	84.7	85.0	1.1
6	950	10.00	3.00	68.3	91.0	0.3
7	1000	10.00	2.00	89.2	78.3	2.1
8	1000	13.00	3.00	75.4	86.9	0.8
9	1000	10.00	4.00	79.7	86.2	1.0
10	1050	10.00	3.00	94.9	66.8	4.1
11	1000	7.00	3.00	93.3	75.7	2.6
12	970	10.00	2.50	77.8	87.4	0.7

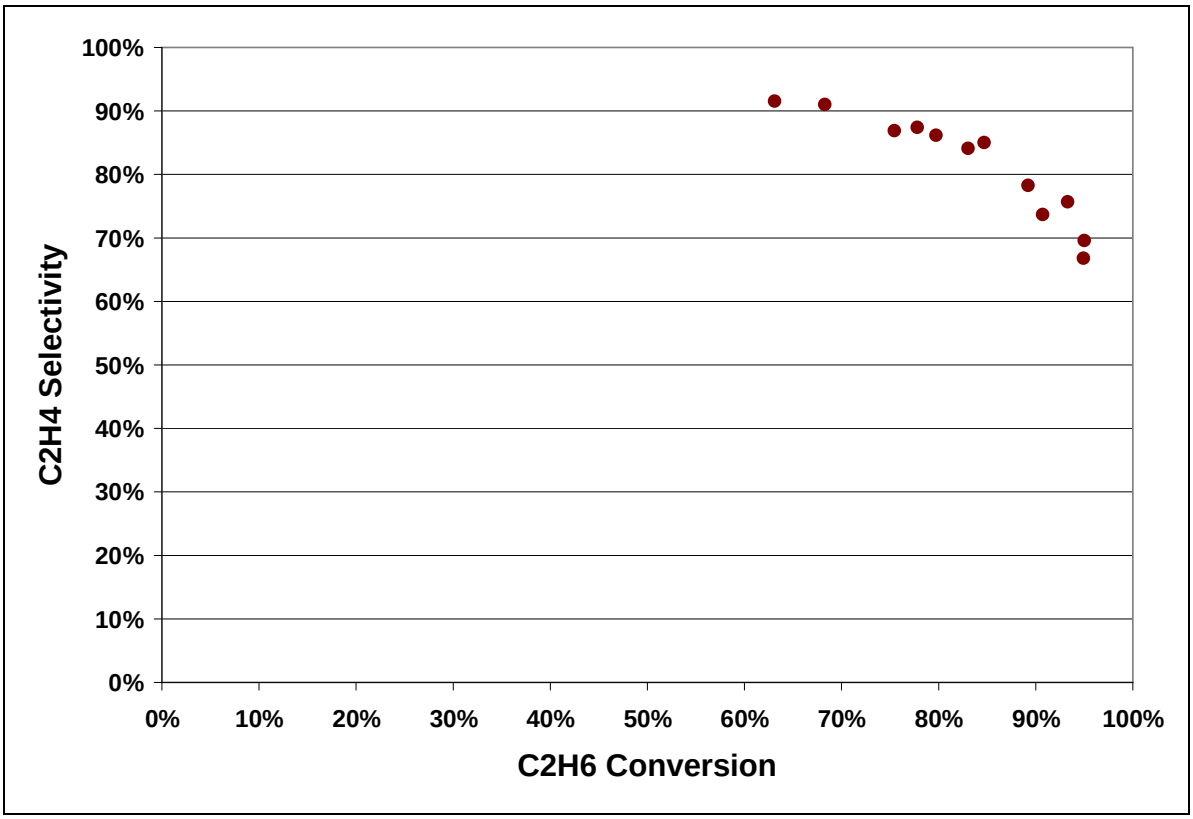

Figure 26 Calculated ethylene selectivity vs. ethane conversion

Collectively, the ethylene selectivity is plotted as a function of ethane conversion in Figure 14.

One of the modeling intents was to optimize the operating conditions to minimize coke formation, while the reactor performance targets of ethane conversion and ethylene selectivity are met. It is important to check the predicted levels of coke formation under various operating conditions. In Figure 27, the C selectivity is shown as a function of the ethane conversion. At higher ethane conversion rates, more coke is predicted to form in the reactor.

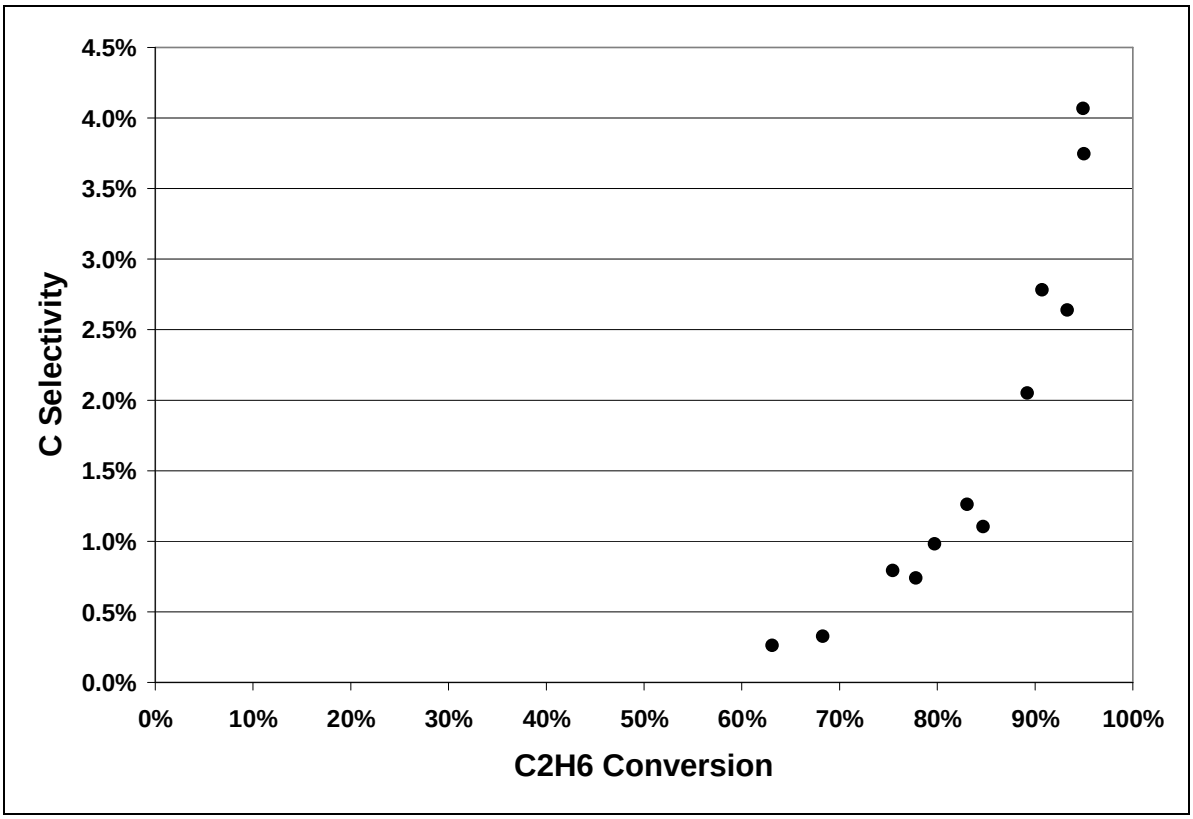

Figure 27 Calculated carbon (coke) selectivity

The model predictions of the reactor performance and levels of the coke formation under various operating conditions of interest provide guidance to explore the optimal operating window within which the targets for ethane conversion and ethylene selectivity are met while the coke formed in the reactor is still below the acceptable level.

Task 9 – Operate Multi-channel Reactor

The first multi-channel reactor that contained a coated Pt-alloy catalyst, was operated for 170 hours. The initial performance was 75% ethane conversion and 80% ethylene selectivity with a total flow rate of 10 SLPM, but over time the selectivity declined to 78%. The thermal profile of the twenty-four channel device was within the range of model predictions. A small increase in dP was observed during the final 10 hours of operation when the process was operated with a lower concentration of H2 in the feed.

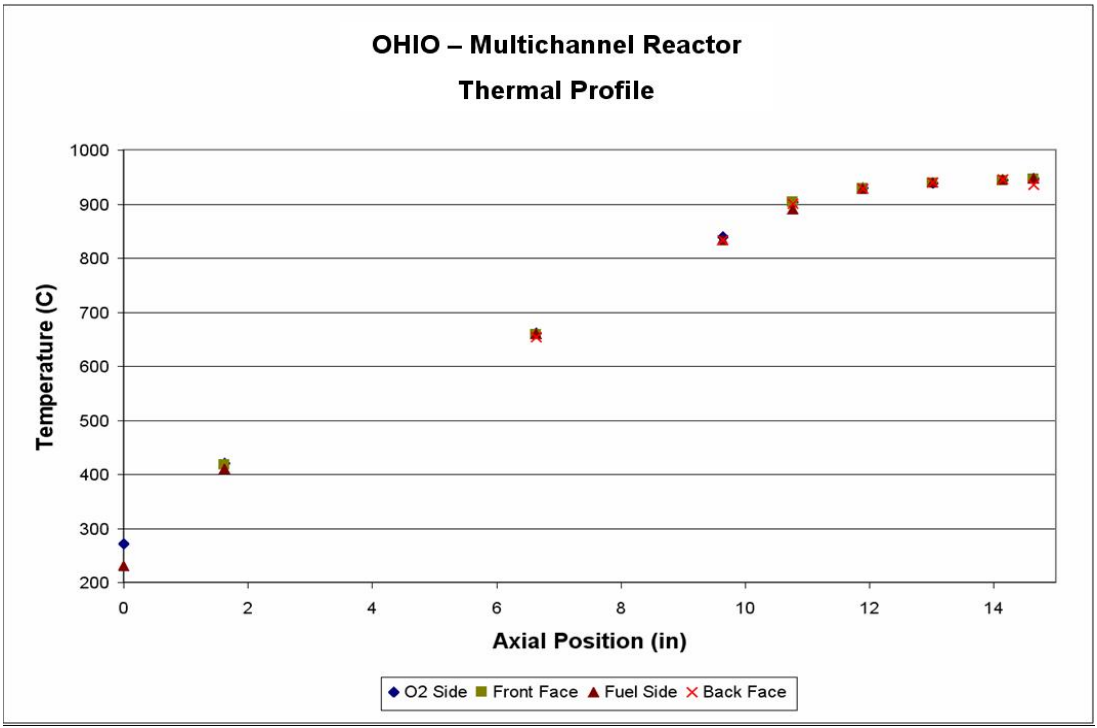

Figure 28. Thermal profile of OHIO multichannel reactor during operation**.**

Several run parameters were modified to try to improve the ethylene selectivity: change in molar percent of hydrogen, change in molar percent of nitrogen flow, and change in total flow rates. None of modifications had positive impact on performance. At approximately 140 hours on stream, the reactor was brought back to its initial condition of 4:4:1 and the performance had dropped to approximately 75% ethane conversion and 78% ethylene selectivity. A drop in oxygen conversion was also noted. Very low selectivities of acetylene were noted throughout the entire run.

Table 5. Performance of OHIO multichannel reactor at 41.5 and 142 hours on stream.

OHIO – Multichannel Reactor

	~One hundred hours between	
hours on stream	**41:28:00**	**142:01:00**
fuel pressure drop	3.7	3.7
O2 pressure drop	3.7	3.6
C2H6 conversion, dry flow basis	75.2%	74.7%
C2H6 conversion, GC basis	**75.0%**	**75.0%**
C2H4 selectivity, GC basis	**80.4%**	**77.9%**
C2H4 selectivity, dry flow basis	79.5%	78.9%
O2 conversion	**99.0%**	**98.1%**
CH4 selectivity, GC basis	7.3%	7.5%
CO selectivity, GC basis	9.0%	9.5%
CO2 selectivity, GC basis	0.8%	0.8%
acetylene selectivity, GC basis	0.0%	0.4%
C3 selectivity, GC basis	1.7%	1.8%
C4 selectivity, GC basis	0.8%	2.1%
Carbon Balance	99.1%	101.0%

The reactor was operated for approximately 170 hours before going through a controlled shut down process. During this time period the reactor pressure drop remained stable up to the last few hours of operation in which a very slight increase in fuel side (ethane/hydrogen) pressure drop was noted. The pressure drop results are summarized in Figure 29.

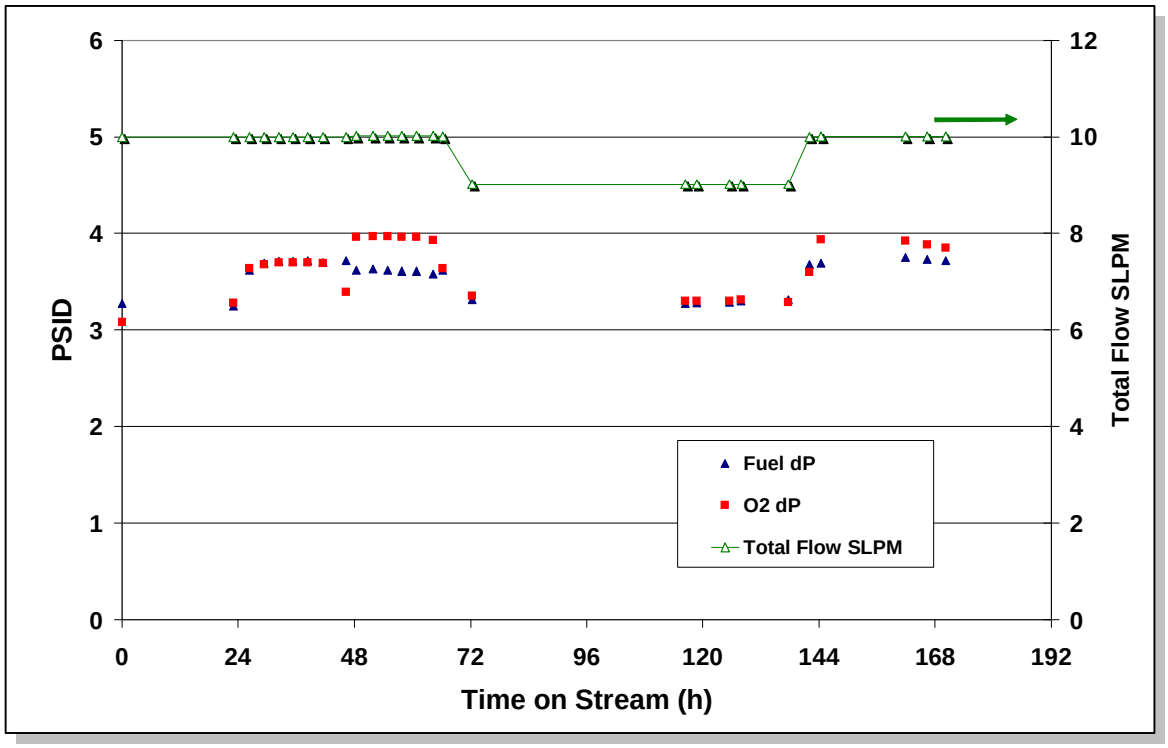

Figure 29. Pressure drop vs time on stream in the OHIO multichannel reactor**.**

The unchanged pressure drops measured in the multichannel device indicate that coke buildup is either very slow or negligible, and the catalyst coating has not blocked the channels to any significant extent.

After cooling under inerts the reactor was removed from the test stand and cut open to expose the surfaces of several channels, and to perform cross section analysis by SEM. This autopsy procedure produced several important observations:

- Coking. Carbon was only observed as a few spots deposited on the wall immediately upstream of the point at which the O2 stream was first mixed with the process gas. There was **no evidence for coke in any of the process or product channels**, or in the reactor exhaust manifold. This indicates that the process produces no measureable coke under the conditions studied since the microchannels remained clear throughout the run, as indicated by the steady dP measurements, and no coke was collected downstream. The minute amount of carbon found in the feed channel may have been the result of a small dead zone, or eddy in the feed stream.

- Protective coating. Cross section SEM analysis of the walls of the multichannel reactor showed that the protective coating applied by Velocys was very uniform and well

adherent to the reactor walls. Samples were evaluated from areas of the reactor that had been exposed to temperatures from room temperature to > 900 C, and all showed uniform coating thickness and no apparent uncoated areas. In a few areas, covering much less than 1% of the surface area, the skin of the coating was cracked, exposing the underlayers. **The protective coating quality was essentially unchanged from that observed with freshly coated surfaces**.

- Catalyst coating. A thin film of the Pt-alloy catalyst was observed in the inlet and outlet manifolds of the reactor, as expected from the coating process used to coat the reactor. In the process channel the catalyst was intact upstream of the O2-process mixing zone, but downstream of the mixing point only minute (1-2 micron) particles of active metal were observed dispersed on the surface. No loose catalyst particles were found downstream or in the manifolds. A few small loose particles rich in Pt were recovered from the O2 feed channel. It thus appears that most of the catalyst evaporated or delaminated from the reactor walls.

Accomplishments

1. A preliminary economic evaluation of the process was completed that shows advantages in both CAPEX and OPEX for the new OHIO process compared to conventional ethane cracking.
2. Adaptation of the conventional fixed bed catalysts to microchannel geometry was demonstrated in small laboratory reactors.
3. Several stabilized catalyst formulations were developed that gave good performance with minimal coke formation and little change in composition with time.
4. A preliminary computational model of the reactor was developed and reconciliation of the kinetic functions was completed.
5. Mod 1 and 2 reactors that include a single full commercial length microchannel were designed, built and operated with high flow rates for more than 100 hours in a continuous run.
6. A multi-channel reactor was designed, built and successfully operated with no apparent buildup of coke or increase in pressure drop. Conversion of ethane and selectivity to ethylene in the reactor nearly matched those observed with the same catalyst in coupon tests. Acetylene production was unusually low.
7. Dow developed a process flowsheet to compare to conventional ethylene processes and identified the advantages of the OHIO process as being largely in the energy/feedstock savings.

Patents: Identify all patents applied for or resulting from this award.

Velocys filed a U.S. patent application, "Catalysts having catalytic material applied directly to thermally-grown alumina and catalytic methods using same; improved methods of oxidataive dehydrogenation," March 23, 2005; Velocys docket number 04-095. The case was subsequently filed in Canada, China, Europe, and Japan.

United States Patent Application Serial Number 11/469,847, "Microchannel Apparatus and Methods of Conducting Catalyzed Oxidative Dehydrogenation" was filed on September 1, 2006.

United States Patent Application Serial Number 11/549,612 and a corresponding PCT application, "Microchannel Apparatus Comprising a Platinum Aluminide Layer and Chemical Processes Using the Apparatus" were filed on October 13, 2006.

United States Patent Application Serial Number 11/670,608, "Process for Making Unsaturated Hydrocarbons Using Microchannel Process Technology" was filed on February 2, 2007. The PCT was subsequently filed on January 31, 2008.

Publications / Presentations: Identify all publications and presentations made for industry or government groups resulting from the award during this quarter.

A public presentation was made at the Spring 2005 AIChE meeting in Atlanta entitled: "Olefins by High Intensity Oxidation" by Terry Mazanec in the Microreaction Technology session on Wednesday April 13, 2005. A copy of the presentation slides was sent to DOE.

A presentation entitled "High Intensity Oxidation of Ethane in a Microchannel Reactor" by T. J. Mazanec*, T. Yuschak, and R. Long was presented by Dr. Mazanec at CatCon2005 on Oct 26, 2005 in Philadelphia, PA. The publication and slides used in the presentation were transmitted to the Project Officer.

A presentation entitled "High Intensity Olefin Production in Microchannel Reactors" by T. J. Mazanec*, T. Yuschak, and R. Long was presented by Dr. Mazanec at AIChE in Orlando on April 26, 2006. The publication and slides for the presentation were transmitted to the Project Officer.

A poster entitled "Catalytic Selective Oxidative Dehydrogenation of Ethane to Ethylene in a Microchannel Reactor" by R. Long, T. Mazanec, F. Daly and T. Yuschak was presented by Dr. Long at the Gordon Research Conference in June 2006. The publication and slides for the presentation were transmitted to the Project Officer.

A presentation entitled "Catalytic Selective Oxidations in Microchannel Reactors" was presented by Terry Mazanec at the 232nd ACS Meeting in San Francisco on September 13, 2006 that included information about the OHIO program that had previously been published and transmitted to the DOE Project Officer.

A presentation entitled "High Intensity Olefin Production in Microchannel Reactors" was made at the Spring AIChE meeting in Houston in April 2007 by Terry Mazanec. The team also participated in the DOE Project Review at the Houston AIChE meeting. The publication and slides for the presentation were transmitted to the Project Officer.

[1] "Energy and Environmental Profile of the U.S. Chemical Industry, May 2000" Energetics Incorporated, Columbia, Maryland for U.S. DOE – OIT, page 48.

[2] Henning, D. A., and L. D. Schmidt, Chemical Eng. Sci. *57* (**2002**) 2615–2625